

**METAL COMPLEXES OF SOME PHENOLIC 1,3-DIKETONES. 1. MONONUCLEAR COMPLEXES OF 1(2-HYDROXYPHENYL)-3-PHENYL-1,3-PROPADIONE AND 1(2-HYDROXYPHENYL)-3(4-METHOXYPHENYL)-1,3-PROPADIONE**

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الخلاصة :

تمّ تصنيع سلسلة من المعقدات الأحادية الفلز لمركبين جديدين من مركبات فينول (١-، ٣- كيتون) . وتم كذلك دراسة خواصها بالتحليل الاولي بالأشعة تحت الحمراء والمطيافية الألكترونية والقابلية المغناطيسية . وعُيِّنَت تراكيب هذه المعقدات على ضوء النتائج السابقة على الصورة  $[ML_2].xS$  حيث إن  $M$  تعني  $VO^{2+}$  ،  $Co^{2+}$  ،  $Ni^{2+}$  ،  $Cu^{2+}$  ،  $UO_2^{2+}$  ، كذلك فإن  $S$  عبارة عن ماء أو أسيتون وقيمة  $x$  تتراوح ما بين ١ و ٥ ، ٣ . كذلك فإن هذه المركبات حُدِّدَت على أنها ثمانية الترتيب ماعدا  $UO_2L_2.1.5C_3H_6O$  ، الذي حُدِّد على أنه سباعي التناسق على صورة هرم ثنائي خماسي الأوجه حول أيون الفلز .

**ABSTRACT**

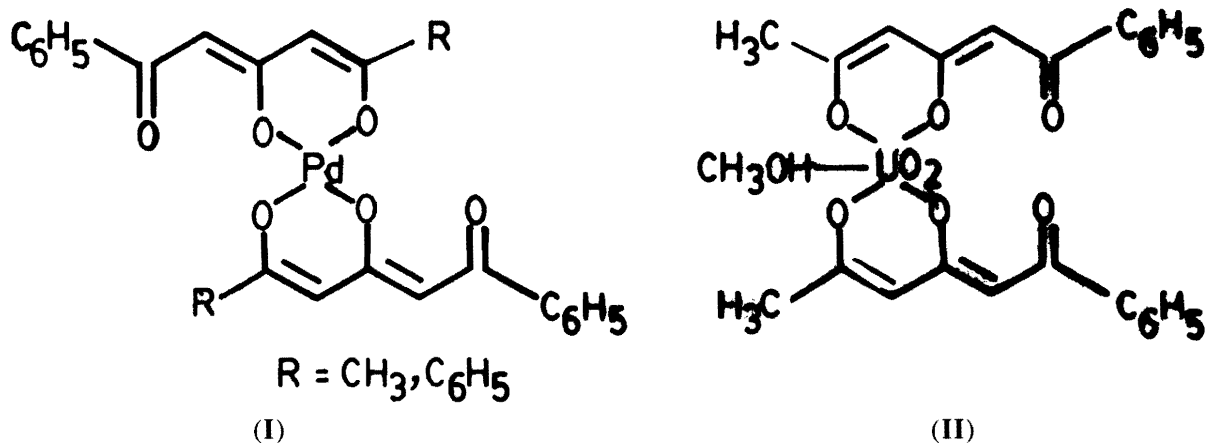
A series of mono-metallic complexes of two new phenolic-1,3-diketones have been synthesized and characterized by their elemental analysis, infra-red and electronic spectra, and magnetic susceptibility. The stoichiometry determined from these results is  $[ML_2].xS$  where  $M = VO^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $UO_2^{2+}$ , and  $S =$  water, acetone and  $x = 1-3.5$ . These complexes have been assigned octahedral structures except  $UO_2L_2.1.5C_3H_6O$ , which has a seven-coordinated pentagonal bipyramidal environment around the metal ion.

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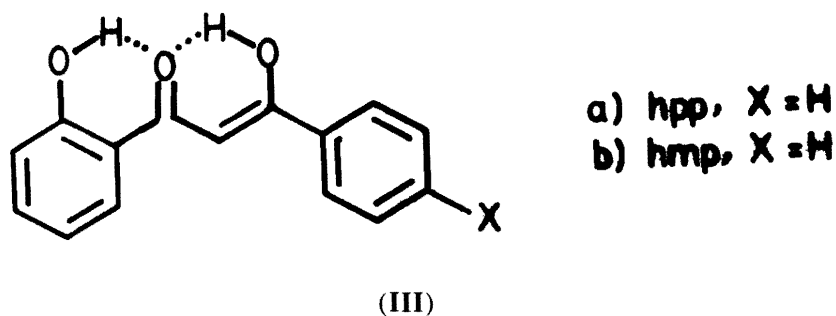
## METAL COMPLEXES OF SOME PHENOLIC 1,3-DIKETONES. 1. MONONUCLEAR COMPLEXES OF 1(2-HYDROXYPHENYL)-3-PHENYL-1,3-PROPADIONE AND 1(2-HYDROXYPHENYL)-3(4-METHOXYPHENYL)-1,3-PROPADIONE

### INTRODUCTION

1,3,5-Triketones and analogous phenolic-1,2-diketones belong to an interesting and versatile class of ligands. These ligands exhibit keto-enol tautomerism and are capable of forming mono- or binuclear complexes, particularly with bivalent metal ions. However, in many cases only bimetallic complexes have been reported [1-3]. A number of workers have investigated antiferromagnetism, cyclic voltammetry and magnetic superexchange phenomenon in these bimetallic complexes [4-6]. Recently, a few monometallic complexes such as Pd(BAA)<sub>2</sub>, Pd(DBA)<sub>2</sub>, and UO<sub>2</sub>(DBA)<sub>2</sub>.CH<sub>3</sub>OH (BAA = 1-Phenyl-1,3,5-hexatriene and DBA = 1,5-Diphenyl-1,3,5-pentatriene) have been reported [7]. These workers assigned a *trans* arrangement of ligands around metal ion in Pd(BAA)<sub>2</sub> and Pd(DBA)<sub>2</sub> (I). Further, *cis*-arrangement of ligands around metal ion in UO<sub>2</sub>(DBA)<sub>2</sub>.CH<sub>3</sub>OH (II) was ascertained through X-ray crystallography [7].



Phenolic-1,2-diketones (III) have identical chelation properties and form mono- and binuclear complexes with transition metal ions. However, only a few copper(II) chelates of 2-acetoacetylphenol have been reported [8]. Mononuclear complexes of phenolic 1,2-diketones with other metal ions have never been reported.



The present investigation was undertaken to synthesize and characterize simple mono-nuclear chelates (in *cis* or *trans* forms) of a series of bivalent metal ions (VO<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and UO<sub>2</sub><sup>2+</sup>) with two new ligands 1(2-hydroxyphenyl)-3-phenyl-1,3-propadiene (hpp) and 1(2-hydroxyphenyl)-3(4-methoxyphenyl)-1,3-propadiene (hmp). The structure elucidation of these chelates based on spectroscopic and magnetic susceptibility

Table 1. Physical Data and Elemental Analyses of Complexes.

S. No.	Compound	Color and Shape***	Method of purification	Yield (%)	m.p./d.p.	Elemental analysis (%)			
						observed (calculated)	C	H	Metal
1	VO(hpp) <sub>2</sub>	Light orange (n)	Recryst.*	81.65	234–38	66.62 (66.07)	4.50 (4.06)	9.16 (9.35)	
2	Co(hpp) <sub>2</sub> · 3.5H <sub>2</sub> O	Light orange (n)	PTLC**	91.8	324	59.55 (60.00)	4.85 (4.87)	10.00 (9.81)	
3	Ni(hpp) <sub>2</sub>	Green (n)	PTLC**	76.54	279–80	67.42 (67.07)	4.68 (4.13)	9.75 (10.92)	
4	Cu(hpp) <sub>2</sub> · 1.5H <sub>2</sub> O	Dark Green (n)	Recryst.*	57.3	301–2	63.05 (63.32)	4.37 (4.37)	11.47 (11.17)	
5	UO <sub>2</sub> (hpp) <sub>2</sub> · 1.5H <sub>2</sub> O	Reddish Orange (c)	PTLC**	90.37	200–2	46.54 (46.46)	3.65 (3.25)	30.69 (30.60)	
6	VO(hmp) <sub>2</sub> · H <sub>2</sub> O	Yellow (p)	Recryst.*	72.44	218–21	59.69 (59.91)	3.95 (4.71)	7.55 (7.94)	
7	Co(hmp) <sub>2</sub> · 3.5H <sub>2</sub> O	Light Orange (n)	PTLC**	84.45	310 (sintered) 324 (melted)	58.36 (58.18)	4.44 (5.03)	8.63 (8.93)	
8	Ni(hmp) <sub>2</sub> · 1.5H <sub>2</sub> O	Dirty Green (n)	PTLC**	74.71	320	61.44 (61.56)	4.07 (4.67)	9.18 (9.40)	
9	Cu(hmp) <sub>2</sub>	Yellowish green (c)	Recryst.*	76.81	295–7	63.61 (63.84)	4.19 (4.35)	9.56 (10.55)	
10	UO <sub>2</sub> (hmp) <sub>2</sub> · 1.5C <sub>3</sub> H <sub>6</sub> O	Reddish Orange (c)	PTLC**	80.4	135–37	49.12 (48.95)	3.82 (3.93)	26.50 (26.53)	

\* Recrystallized from DMF/methanol

\*\* Preparative thin layer chromatography on silica gel plates (60 HF<sub>254</sub> · E. Merck) of 1 mm thickness with acetone–pet. ether 93:7, v/v)

\*\*\* n = needles, c = crystals, p = powder.

measurements has been discussed. Synthesis of these ligands *via* the Baker–Venkataramen rearrangement has already been reported [9].

## EXPERIMENTAL

All the reagents used were of AR grade and were used without further purification. The ligands were prepared by a method reported earlier [9].

The chelates were prepared by the following general procedure: To a stirred solution of the ligand (2 mmol) in acetone was added an aqueous solution of the metal acetate (1.2 mmol) while keeping the temperature below  $-5^{\circ}\text{C}$ . The reaction mixture was then adjusted to pH 9 with aqueous ammonia. After stirring for  $\frac{1}{2}$  h at  $0^{\circ}\text{C}$  and 1 h at room temperature, cold water was added to precipitate out the chelate, which was filtered, washed with water to remove the inorganic salts, and dried in vacuum.

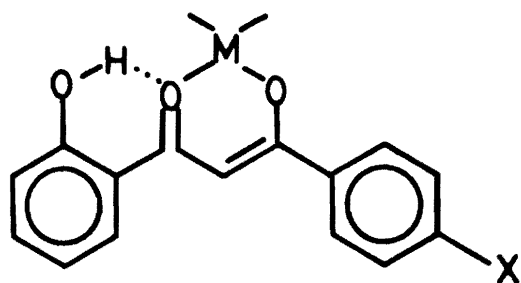
The complexes of  $\text{Cu}^{2+}$  and  $\text{VO}^{2+}$  were recrystallized from DMF/methanol (1:1) while complexes of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{UO}_2^{2+}$  were purified by preparative thin-layer chromatography, carried out on 1 mm thick silica gel plates (60 HF<sub>254</sub>, E. Merck) using acetone:pet. ether 3:7, v/v as eluent. The colored zones were scratched from the plates, extracted with acetone, evaporated to minimum volume and kept for crystallization after addition of a small volume (5 ml) of methanol. The physical data of all these complexes are summarized in Table 1.

Metal contents of these complexes were determined by reported spectrophotometric methods; nickel(II) with dimethylglyoxime, cobalt(II) with nitroso-*R*-salt and vanadium(IV) with hydrogen peroxide while copper(II) was determined by an electrogravimetric method [10]. The uranium contents of the complexes were estimated by inductively coupled plasma atomic emission spectrometric set up (ICP-AES) consisting of a JY-38 VHR monochromator and a JY-48 polychromator, using wavelength 385.958 nm [11]. The melting points were determined on a Gallenkamp digital melting point apparatus and the C, H analyses were carried out on Carlo-Erba model DM-200. For recording IR spectra, KBr discs were used on Hitachi model 270-50 spectrophotometer. UV spectra were recorded on a Shimadzu model 265 FS/FW spectrophotometer. For magnetic susceptibility measurements Gouy's method was employed. The apparatus consists of a water cooled electro-magnetic MSB-10 manufactured by Chyo Corporation Japan, attached to a Mettler H-55 balance. The data are tabulated in Tables 1–4.

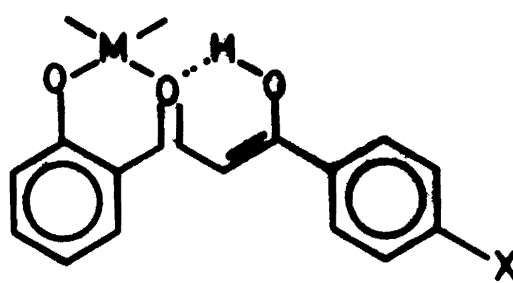
## RESULTS AND DISCUSSION

A series of ten mononuclear complexes of bivalent metal ions such as  $\text{VO}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{UO}_2^{2+}$  with two new ligands 1(2-hydroxyphenyl)-3-phenyl-1,3-propadione and 1(2-hydroxyphenyl)-3-(4-methoxyphenyl)-1,3-propadione (hmp) were synthesized. Although these ligands are capable of binding two metal ions forming  $\text{M}_2\text{L}_2$  complexes with oxygen bridges, simple mononuclear chelates were prepared by reacting the appropriate quantities of metal ions with ligands in methanol or acetone solution at low temperature ( $-5 - 0^{\circ}\text{C}$ ). If the reactions were carried out at higher temperatures, binuclear species were precipitated as the main product. The chelates were obtained in fairly good yield (72–92%) and were purified by recrystallization or preparative TLC (Table 1). Elemental analysis (Table 1) of these complexes indicate that one metal ion is bound to two ligands with  $[\text{ML}_2] \cdot x\text{H}_2\text{O}$  ( $x = 1-3.5$ ) stoichiometry. The  $[\text{UO}_2(\text{hmp})_2]$  complex is associated with 1.5 molecules of acetone. These complexes decompose between  $135-324^{\circ}\text{C}$ ,  $[\text{UO}_2(\text{hmp})_2] \cdot 1.5\text{C}_3\text{H}_6\text{O}$  being the least stable and decomposing at  $135^{\circ}\text{C}$ . They are fairly soluble in various organic solvents such as acetone, chloroform, benzene, and DMF. As such a number of these complexes were recrystallized from DMF/methanol yielding microcrystalline products.

The infrared spectra (Table 2) of these complexes show split bands at  $1606-26\text{ cm}^{-1}$  and  $1584-96\text{ cm}^{-1}$  indicating the presence of enolic carbonyl. In addition one or two additional bands at  $1557-63$  and  $1518-27\text{ cm}^{-1}$  assigned to stretching vibrations of coordinated carbonyl have been observed. These ligands are capable of binding a metal ion in two positions (IV & V).



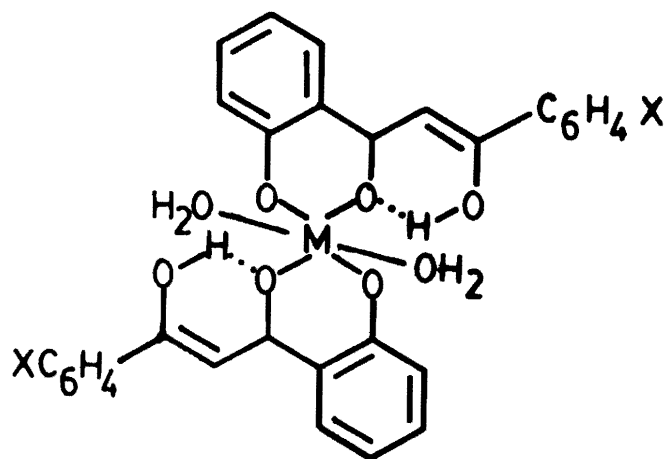
(IV)



(V)

The presence of bands due to stretching vibrations of coordinated carbonyl as well as enolic carbonyl indicate that phenolic oxygen atoms are bonded to the metal ions as in V. Other peaks in IR spectra indicate the stretching vibrations due to conjugated diolefin C=C between  $1575\text{--}1596\text{ cm}^{-1}$ , stretching vibrations due to C=C and C-H between  $1465\text{--}1500\text{ cm}^{-1}$ , and in-plane bending of C-H between  $1296\text{--}1305\text{ cm}^{-1}$ . The vanadyl and uranyl chelates show bands between  $903\text{--}906\text{ cm}^{-1}$  and  $908\text{--}915\text{ cm}^{-1}$  due to V=O and U=O stretching vibrations respectively.

The electronic spectra of these compounds, when compared with electronic spectra of *bis(o*-hydroxyacetophenolato) copper(II) and *bis*(2-acetoacetylphenolato) copper(II), indicate that chelation involves the phenolic groups. The former model compound which resembles chelate IV showed two bands at  $15\,924\text{ cm}^{-1}$  and  $17\,688\text{ cm}^{-1}$ , and the later which is analogous to chelate V showed only one band at  $14\,706\text{ cm}^{-1}$ . The electronic spectra of the newly synthesized chelates  $[\text{Cu}(\text{hpp})_2] \cdot 1.5\text{ H}_2\text{O}$  and  $[\text{Cu}(\text{hmp})_2]$  in DMF consist of only a single band at  $15\,332\text{ cm}^{-1}$  and  $15\,361\text{ cm}^{-1}$  respectively, indicating that the structure V is the most probable structure. The *trans* arrangement of the two ligands around the metal ions is more probable because *cis* structure suffers from the steric hindrance of phenolic protons. Attempts to incorporate a second metal ion to give heterobinuclear complexes failed with some of these complexes. This also indicates the *trans* arrangement of the ligands around the metal ion as shown in VI.



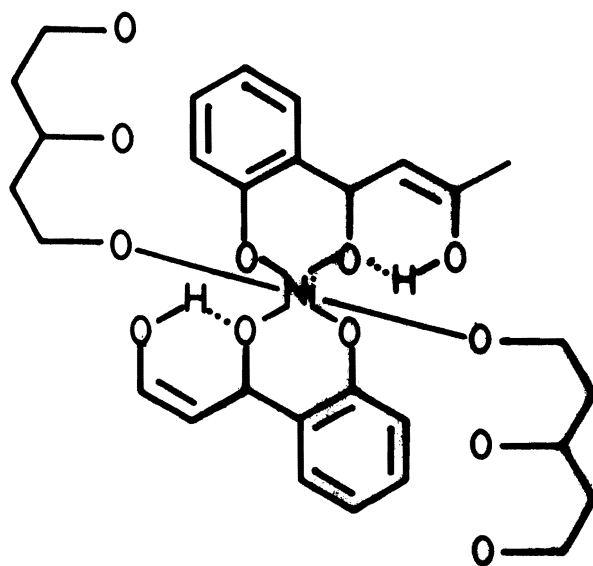
(VI)

Table 2. Infrared Spectral Data for Solid Complexes in (KBr) Disk  $\nu_{\max} \text{ cm}^{-1}$ .

S. No.	Compound	$\nu_{\text{C=O}}$ enol	$\nu_{\text{C=C}}$ conjg olefinic	$\nu_{\text{C=O}}$ (coord)	$\nu_{\text{C=C}}$ + $\nu_{\text{C-H}}$	C-H bending of CH-C=O	$\nu_{\text{C=O}}$ + C-H bending	C-H in plane bending	M=O
1	hpp	1608 (s)	1575 (s)	-	1491 (s)	1440 (m) 1416 (m)	1305 (s)	1197 1188 (s,d)	-
2	VO(hpp) <sub>2</sub>	1623 (s)	1590 (m)	-	1491 (s) 1467 (s)	1437 (m) 1383 (s)	1302 (s)	1200 (s)	903
3	Co(hpp) <sub>2</sub> · 3.5H <sub>2</sub> O	1620 (w)	1596 (s)	1557 (w) 1518 (s)	1488 (s)	1440 (w) 1413 (w)	1296 (m)	1206 (m)	-
4	Ni(hpp) <sub>2</sub>	1620 (s)	1596 (s)	1563 (w) 1518 (s)	1488 (s) 1473 (s)	1440 (m) 1419 (w)	1314 (w) 1296 (s)	1206 (m)	-
5	Cu(hpp) <sub>2</sub> · 1.5H <sub>2</sub> O	1620 (s)	1590 (s)	1563 (sh) 1550 (sh)	1488 (s) 1464 (s)	1437 (m) 1395 (m)	1314 (s)	1230 (s)	-
6	UO <sub>2</sub> (hpp) <sub>2</sub> · 1.5H <sub>2</sub> O	1620 (m)	1593 (s)	1538 (sh) 1518 (s)	1488 (s) 1464 (m)	1437 (m) 1371 (w)	1290 (s)	1200 (s)	909
7	hmp	1617 (s) 1605 (s)	1572 (s) 1515 (m)	-	1491 (s)	1433 (s) 1407 (w)	1320 (s)	1242 (s)	-
8	VO(hmp) <sub>2</sub> · H <sub>2</sub> O	1608 (s)	1584 (m)	1575 (sh) 1547 (m) 1525 (w)	1497 (s)	1392 (m)	1299 (s)	1266 (s) 1203 (s)	906
9	Co(hmp) <sub>2</sub> · 3.5H <sub>2</sub> O	1607 (s)	1575 (sh)	1526 (m)	1499 (s)	1394 (m)	1301 (s)	1256 (s)	-
10	Ni(hmp) <sub>2</sub> · 1.5H <sub>2</sub> O	1609 (s)	1593 (s)	1527 (s)	1500 (s)	1404 (s)	1299 (s)	1257 (s) 1202 (s)	-
11	Cu(hmp) <sub>2</sub>	1617 (s) 1605 (sh)	1587 (sh)	1575 (s) 1509 (s)	1491 (s)	1443 (m) 1407 (w)	1302 (s)	1242 (s) 1197 (s)	-
12	UO <sub>2</sub> (hmp) <sub>2</sub> · 1.5C <sub>3</sub> H <sub>6</sub> O	1606 (s)	1587 (s)	1527 (s)	1497 (s)	1416 (w)	1305 (s)	1260 (s) 1203 (m)	915

s = strong, m = medium, w = weak, sh = shoulder, d = doublet.

The magnetic moments (Table 3) of these chelates are typical of mononuclear species. The  $\text{VO}^{2+}$  and  $\text{Cu}^{2+}$  complexes have their moments between 1.78–2.06 BM and 1.93–1.95 BM respectively, as expected for one unpaired electron in these systems. The  $\text{Co}^{2+}$  complexes have magnetic moments between 4.95–4.96 BM typical of three unpaired electrons in a  $d^7$  system. These higher values of magnetic moments are indicative of an appreciable contribution from orbital angular momentum. Usually octahedral complexes of  $\text{Co}^{2+}$  ion have moments between 4.8–5.1 BM. The observed magnetic moments of the present series of complexes suggest that cobalt(II) ion has an octahedral environment of donor atoms which is only possible through *trans* coordination of two water molecules as shown in VI. Similarly the nickel(II) chelates are paramagnetic with magnetic moments between 2.93–3.17 BM values indicating the presence of two unpaired electrons. The paramagnetic moments of these nickel(II) chelates indicate six coordination around the metal ion because the four coordinated species in a square planar array are usually diamagnetic. The elemental analysis of these complexes do not permit six coordination since no solvent is associated with these nickel complexes. However, nickel(II) ion in these complexes may be six coordinated through bonding with two donor carbonyl oxygen atoms of neighboring chelates as shown in VII. As expected the uranyl complexes are diamagnetic due to completely filled  $d$  and empty  $f$  orbitals in the uranium(VI) ion.



(VII)

The electronic spectra (Table 4) of these complexes in DMF solution consist of single bands between 13 068–18 018  $\text{cm}^{-1}$  ( $\epsilon = 6.97\text{--}73.92 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the  $d\text{--}d$  transition region and two very intense bands between 25 227–27 447  $\text{cm}^{-1}$  ( $\epsilon = 3.46\text{--}5.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). The uranyl complexes although red colored have no absorption in visible region of the spectrum mainly due to completely filled lower  $d$ -orbitals. The very strong charge transfer bands of the uranyl complexes extend well into visible region imparting color to these species. The UV absorption spectra of other complexes consist of single intense bands between 26 469–27 027  $\text{cm}^{-1}$  ( $\epsilon = 4\text{--}5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), which may be assigned to ligand  $\rightarrow$  metal charge transfer transition. The absorption spectrum of  $[\text{UO}_2(\text{hpp})_2] \cdot 1.5 \text{ H}_2\text{O}$  consists of two bands at 25 432  $\text{cm}^{-1}$  and 27 397  $\text{cm}^{-1}$  while that of  $[\text{UO}_2(\text{hmp})_2] \cdot 1.5 \text{ C}_3\text{H}_6\text{O}$  has only one band at 25 291  $\text{cm}^{-1}$ . The higher energy band in former complex is comparable to that observed for rest of the complexes in the series and may be assigned to  $\text{L} \rightarrow \text{M}$  charge transfer. The second lower energy band in both of these complexes is perhaps a second  $\text{L} \rightarrow \text{M}$  charge transfer band. Since uranium(VI) is in a higher oxidation state, it can easily accept an electron from the donor atom with a resultant low energy charge transfer.

The crystal field spectra of  $\text{VO}^{2+}$  and  $\text{Cu}^{2+}$  complexes consist of single broad bands between 13 068–13 082  $\text{cm}^{-1}$  and 15 332–15 361  $\text{cm}^{-1}$ , respectively. This band arises from the excitation of an electron from lower  ${}^2T_{2g} \rightarrow {}^2E_g$  state ( ${}^2E_g \rightarrow {}^2T_{2g}$  for  $\text{Cu}^{2+}$  complex) assuming an octahedral environment around these metal ions. Similarly, single

**Table 3. Magnetic Susceptibility Data for Solid Complexes.**

S. No.	Compound	Molecular wt.	$\chi_g \times 10^{-6}$ c.g.s.	$\chi_M \times 10^{-6}$ c.g.s.	$\chi_M \times 10^{-6}$ (corrected) c.g.s. units	$\mu_{\text{eff}}$ B.M.
1	VO(hpp) <sub>2</sub>	545.44	1.921	1047.53	1316.55	1.78
2	Co(hpp) <sub>2</sub> · 3.5H <sub>2</sub> O	660.461	16.552	9789.23	10102.3	4.95
3	Ni(hpp) <sub>2</sub>	537.19	6.095	3274.17	3587.24	2.93
4	Cu(hpp) <sub>2</sub> · 1.5H <sub>2</sub> O	569.05	2.249	1279.79	1573.30	1.95
5	UO <sub>2</sub> (hpp) <sub>2</sub> · 1.5H <sub>2</sub> O	775.53		diamagnetic		
6	VO(hmp) <sub>2</sub> · H <sub>2</sub> O	641.50	2.241	1437.60	1766.56	2.06
7	Co(hmp) <sub>2</sub> · 3.5H <sub>2</sub> O	660.51	15.011	9914.93	10260.89	4.96
8	Ni(hmp) <sub>2</sub> · 1.5H <sub>2</sub> O	624.24	6.020	3872.54	4199.54	3.17
9	Cu(hmp) <sub>2</sub>	602.10	2.07	1246.34	1553.30	1.93
10	UO <sub>2</sub> (hmp) <sub>2</sub> · 1.5C <sub>3</sub> H <sub>6</sub> O	895.58		diamagnetic		

**Table 4. Absorption Band Positions and Extinction Coefficients for the Complexes, Measured in Dimethylformamide Solution.**

Sample Number	Compound	$\lambda_{\text{max}} \text{ cm}^{-1}$ ( $\epsilon \text{ mole}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$ )	
1	VO(hpp) <sub>2</sub>	26 695 ( $4.27 \times 10^4$ ),	13 068 (16.36)
2	Co(hpp) <sub>2</sub> · 3.5H <sub>2</sub> O	27 337 ( $5.20 \times 10^4$ ),	18 018 (50.03)
3	Ni(hpp) <sub>2</sub>	27 056 ( $4.19 \times 10^4$ ),	15 704 (6.97)
4	Cu(hpp) <sub>2</sub> · 1.5H <sub>2</sub> O	27 427 ( $4.8 \times 10^4$ ),	15 332 (30.82)
5	UO <sub>2</sub> (hpp) <sub>2</sub> · 1.5H <sub>2</sub> O	27 397 ( $3.47 \times 10^4$ ),	25 432 ( $2.76 \times 10^4$ )
6	VO(hmp) <sub>2</sub> · H <sub>2</sub> O	26 469 ( $4.18 \times 10^4$ ),	13 082 (20.4)
7	Co(hmp) <sub>2</sub> · 3.5H <sub>2</sub> O	27 263 ( $5.15 \times 10^4$ ),	18 116 (52.74)
8	Ni(hmp) <sub>2</sub> · 1.5H <sub>2</sub> O	26 853 ( $5.03 \times 10^4$ ),	15 654 (8.75)
9	Cu(hmp) <sub>2</sub>	26 724 ( $4.87 \times 10^4$ ),	15 301 (38.62)
10	UO <sub>2</sub> (hmp) <sub>2</sub> · 1.5C <sub>3</sub> H <sub>6</sub> O	25 291 ( $3.47 \times 10^4$ )	

The electronic spectra of octahedral Ni<sup>2+</sup> complexes usually consist of several bands in visible region. However a band observed between 12 530–19 800 cm<sup>-1</sup> has been assigned to electronic transition  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  by a number of earlier researchers [12]. Further, the single band between 18 018–18 116 cm<sup>-1</sup> observed in crystal field spectra of Co<sup>2+</sup> complexes may be assigned to a spin allowed transition  ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$  in an octahedral environment. This is in good agreement with bands that have been reported earlier [12].

These studies indicate that metal ions in these series of chelates are six coordinated and have octahedral environment. All these chelates except [VO(hpp)<sub>2</sub>], [Ni(hpp)<sub>2</sub>], and [Cu(hmp)<sub>2</sub>] are associated with 1–3 water molecules, two of which occupy *trans* positions, as shown in VI. The metal ions with [ML<sub>2</sub>] and [ML<sub>2</sub>].H<sub>2</sub>O stoichiometry may be coordinated to oxygen atoms of the neighboring carbonyl part of the ligands, thus achieving six coordination as shown in VII. The uranyl complexes are associated with solvent molecules achieving the preferred seven coordinated pentagonal bipyramidal environment.



The preceding discussion clearly indicates the great potential of phenolic-1,3-diketones in complex formation. The presence of other substituents in the *para* position on the phenyl ring has very little effect upon their complex-forming ability.

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