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Synthesis and Properties of Some Metal Complexes and Organometallic Compounds of Phthalic Acid

MAMTA SINGH and RAM NAYAN*
Department of Chemistry
Hindu College, Moradabad-244 001, India

Metal complexes $[CuL\cdot 2H_2O\cdot 2DMF]$ (I), $Na_2[CuL_2\cdot 2H_2O]\cdot 4DMF$ (II), $Na_4[CuL_3]\cdot 5DMF$ (III), $[CuL\cdot 2DP]\cdot 2DMF$ (IV), $Na_2[CuL_2\cdot DP]\cdot 5DMF$ (V), $[NiL\cdot 2H_2O\cdot 2DMF]$ (VI), $Na_2[NiL_2\cdot DMF]$ (VII), $Na_4[NiL_3]\cdot 3.5DMF$ (VIII), $[NiL\cdot 2DP]\cdot 0.5DMF$ (IX) and $Na_2[NiL_2\cdot DP]\cdot DMF$ (X) (where L, DMF and DP are phthalate dianion, dimethylformamide and 1,3-diaminopropane, respectively) and organometallic compounds $Cu(C_7H_4O_2)\cdot(2H_2O)$ (XI), $Ni(C_7H_4O_2)(2H_2O)$ (XII) and $Zn(C_7H_4O_2)(DMF)$ (XIII) (derived from phthalic acid) have been prepared andd characterised by elemental analysis, conductivity measurements and spectral studies.

INTRODUCTION

Metal derviatives of phthalic acid have not been extensively studied in spite of the fact that they exhibit fungicidal and bacteriocidal properties[1–3] as well as catalytic activities[1, 3–5] and show unusual metal-ligand bonding depending upon their preparation methods[6–8]. Some mixed ligand complexes with polymeric infinite chains have also been reported. In addition, the organometallic compound of phthalic acid with molecular formula $C_7H_4O_2\cdot Hg$ is formed when mercuric acetate is fused with the ligand or mercury salt of phthalic acid is heated[9].

The aim of the present work, in view of the diversity observed in the structures of the phthalic acid compounds, is to prepare binary complexes of phthalic acid with Ni^{2+}, Cu^{2+} and Zn^{2+} ion refluxing their mixtures in DMF, and subsequently to obtain their mixed lignand complexes by treating the resulting complexes with 1,3-diaminopropane. Attempts have also been made to prepare some organometallic compounds.

EXPERIMENTAL

Phthalic acid (Merck), 1,3-diaminopropane (G.E.C.), dimethylformamide (B.D.H.), benzene (Glaxo) and analytical grade metal salts were used in this work. Analyses for carbon, hydrogen and nitrogen were performed at the Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh. For obtaining the metal percentage in the complexes their known amounts were decomposed by usual methods and the metal contents were estimated by EDTA titration procedure[10]. The conductivity measurements data were recorded using 10^{-2} M solution with the help of D.D.R. conductivity meter, type 304. Infrared spectra in the range 4000-400 cm^{-1} were recorded by using infrared spectrophotometer (Perkin-Elmer, FTIR) at IIT, New Delhi.

Preparation of Compounds

Binary Complexes: Mixtures of metal acetate (Cu^{2+} and Ni^{2+}) and phthalic acid (5.0 g in each case) in 1 : 1 molar ratio were prepared in 150 mL dimethyl formamide, and were refluxed for 3–4 h till the bluish green and green precipitates of the Cu^{2+} and Ni^{2+} compounds, respectively were obtained. The complexes ($CuL{\cdot}2H_2O{\cdot}2DMF$ and $NiL{\cdot}2H_2O{\cdot}2DMF$) were filtered and washed with dimethylformamide. Solvent content was reduced by treating the compounds with benzene. Finally, the metal complexes were dried at 100°C temperature under reduced pressure. Presence of H_2O molecule in the compounds prepared in nonaqueous medium is expected due to coordination of H_2O molecule available from hydrated metal acetate/atmospheric moisture.

For preparation of 1 : 2, metal-phthalic acid complexes, 1 : 1 : 1 molar mixtures of metal (Ni^{2+} and Cu^{2+}) acetate, phthalic acid (6.0 g in each metal system) and its disodium salt in 150 mL DMF were refluxed, for 4–5 h. The coloured solids ($Na_2[CuL_2{\cdot}2H_2O]{\cdot}4DMF$ and $Na_2[NiL_2{\cdot}2DMF]$) were filtered, washed and dried as described for 1 : 1, metal-ligand complexes.

Mixtures of nickel acetate or copper acetate with phthalic acid and its disodium salt were again refluxed by keeping the molar ratio 1 : 1 : 2 for 4–5 h to obtain 1 : 3, metal-ligand complexes ($Na_4[CuL_3]{\cdot}5DMF$, $Na_4[NiL_3]{\cdot}3.5DMF$).

Attempt to synthesize Zn^{2+} complexes could not be materialised due to their thermal instability at boiling DMF leading to the formation of organometallic compound.

Mixed Ligand Complexes: 1 : 1 and 1 : 2, metal-phthalic acid complex species were treated in cold with an excess amount of 1,3-diaminopropane (DP) with constant stirring for about 4 h. A sharp change in colours in each case confirms the formation of mixed complexes. The resulting solids ($[CuL{\cdot}2DP]{\cdot}2DMF$ (greenish black), $Na_2[CuL_2{\cdot}DP]{\cdot}5DMF$ (violet), $[NiL{\cdot}2DP]{\cdot}0.5DMF$ (light blue) and $Na_2[NiL_2{\cdot}DP]{\cdot}DMF$ (very light blue) were dried under reduced pressure to remove the excess of 1,3-diaminopropane.

Organometallic compounds: The compounds $[CuL{\cdot}2H_2O{\cdot}2DMF]$, $Na_2[CuL_2{\cdot}2H_2O]{\cdot}4DMF$, $Na_4[CuL_3]{\cdot}5DMF$ and $[NiL{\cdot}2H_2O{\cdot}2DMF]$ on heating at *ca.* 300°C in absence of oxygen and subsequently treating with water yield organometallic compounds $Cu(C_7H_4O_2)(2H_2O)$ and $Ni(C_7H_4O_2)(2H_2O)$. The compounds were dried under reduced pressure. The possible structural changes as a result of heating the binary complexes are given in Fig. 1 (a–c). Liberation of phthalic anhydride in Fig. 1 (b and c) is inferred from the smell of the anhydride evolved during heating and its depositoon on the walls of the heating vessel on cooling.

Mixture of 6.6059 g zinc acetate and 5.0 g phthalic acid (1 : 1, molar ratio) refluxed for 3 h in dimethylformamide yields organometallic compound $Zn(C_7H_4O_2)(DMF)$. The compound was dried and purified similar to binary complexes of the ligand with Cu^{2+} and Ni^{2+}.

RESULTS AND DISCUSSION

The complexes and organometallic compounds, reported in Table-1, have been

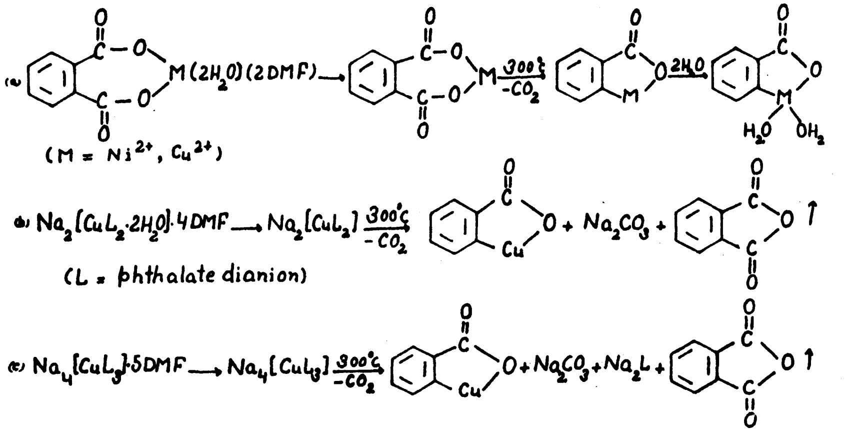

Fig. 1 Proposed scheme for formation of organometallic compounds of Cu^{2+} and Ni^{2+}

characterised on the basis of results of elemental analysis, solubility, conductivity and IR spectra. The infrared spectra of all the complexes give a clear view for their structures. A most favourable peak appearing due to ν(M—O) gives a confirmative support for their proposed structures. The absence of bands due to important functional groups of phthalic acid is a convincing proof of the cooordination of oxygen to the metal in all the complexes. Assuming that the metal ion adopts normally preferred geometry in their complexes, the analytical data are also suggestive of the stoichiometry proposed for the complexes. The metal complexes are slightly soluble in organic solvents, ethanol, methanol, DMF, DMSO, etc. (except orgnometallic compounds which are very slightly soluble only in DMF and DMSO). Complexes (I), (IV), (VI) and (IX) are moderately soluble in water while (XI)–(XIII) are practically insoluble. Compounds (II), (III), (V), (VII) and (VIII), (X) being ionic in nature are highly soluble in aqueous medium.

Infrared spectra of phthalate complexes: The infrared spectra of the complexes, (I), (II) and (VI) or (III), (VII), (VIII) or (IV), (V), (IX), (X) separately do not show any significant change. However, the bands observed in pure phthalic acid at frequencies (cm^{-1}) 2850 (s, b, —OH hydrogen bonded), 1970 (m, >C═O stretching), 1440 (m, sp) and 1270 (m, sp) coupled vibration (involving C—O stretching and —OH in plane deformation), 900 (m, sp, out-of-plane deformation (wag) vibration for O—H) are missing in all the complexes. The conclusive evidence of bonding of the ligand to the metal ions through oxygen donor is provided by the presence of bands (cm^{-1}) at 472 (m, sp), 456 (m, sp), 496 (s, b), 472 (w, sp), 488 (w, sp), 460 (m, sp), 450 (m, sp), 480 (s, b), 468 (w, sp) and 480 (w, sp) attributed to ν(M—O), respectively in (I)–(X) complexes[11]. The presence of coordinated water molecules in the complexes (I), (II) and (VI) is indicated by the appearance of medium bands at 3456, 3456 and 3460 cm^{-1}, respectively, attributed to O—H stretching, followed by strong and sharp peaks appearing in the region 850–840 cm^{-1} (rocking vibrations) and 730–770 cm^{-1} (wagging vibrations)[12]. Sharp peaks at 658, 654 and 646 cm^{-1} in (I) , (II) and (VI) complexes, respectivley, suggest the coordination of oxygen to metal ion (ν(M—O). H_2O)[13, 14].

TABLE-1
ANALYTICAL AND PHYSICAL DATA FOR COPPER(II), NICKEL(II) AND ZINC(II) COMPLEXES

Compound*	Colour	Molar conductivity (ohm^{-1} cm^2 mol^{-1})	% Found (Calcd.)			
			M	C	H	N
[$CuL·2H_2O·2DMF$] (I)	Bluish green	20	15.58 (15.53)	41.27 (41.07)	6.08 (6.11)	6.82 (6.84)
$Na_2[CuL_2·2H_2O]·4DMF$ (II)	Light blue	280	8.33 (8.30)	43.70 (43.89)	5.21 (5.22)	7.30 (7.31)
$Na_4[CuL_3]·5DMF$ (III)	Greenish blue	400	6.30 (6.28)	46.11 (46.29)	4.61 (4.64)	6.90 (6.92)
[CuL·2DP]·2DMF (IV)	Greenish black	30	12.25 (12.19)	45.94 (46.06)	7.27 (7.29)	21.47 (21.49)
$Na_2[CuL_2·DP]·5DMF$ (V)	Violet	380	7.27 (7.25)	46.48 (46.57)	6.04 (6.05)	11.20 (11.18)
[$NiL·2H_2O·2DMF$] (VI)	Green	40	14.39 (14.35)	41.68 (41.58)	5.42 (5.44)	6.93 (6.93)
$Na_2[NiL_2·2DMF]$ (VII)	Yellowish green	350	9.98 (10.03)	45.58 (45.67)	3.98 (3.98)	4.83 (4.84)
$Na_4[NiL_3]·3.5DMF$ (VIII)	Yellow	450	6.41 (6.44)	46.23 (46.13)	4.06 (4.07)	5.23 (5.24)
[NiL·2DP]·0.5DMF (IX)	Light blue	50	14.23 (14.28)	45.68 (45.83)	6.79 (6.77)	15.54 (15.51)
$Na_2[NiL_2·DP]·5DMF$ (X)	Very light blue	360	9.98 (10.00)	45.48 (45.50)	4.33 (4.31)	6.99 (7.00)
$Cu(C_7H_4O_2)(2H_2O)$ (XI)	Brown	—	28.91 (29.01)	38.35 (38.31)	3.65 (3.65)	—
$Ni(C_7H_4O_2)(2H_2O)$ (XII)	Brown	—	27.01 (27.10)	39.14 (39.25)	4.66 (4.67)	—
$Zn(C_7H_4O_2)(DMF)$ (XIII)	Blackish white	—	25.19 (25.30)	46.45 (46.44)	4.25 (4.25)	5.40 (5.41)

*L = phthalate dianion.

Sharp bands of strong intensity centered at 3312, 3264 cm^{-1}; 3312, 3200 cm^{-1}; 3324, 3280 cm^{-1}; 3328, 3216 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of NH_2 group respectively, in the complexes (IV), (V), (IX) and (X). These bands appear at lower frequencies than in the free amine ligand. This effect is a convincing proof of the coordination of the amine group[15, 16]. It is further confirmed by the other evidence of bonding of the ligand to the metal ion, obtained tentatively by the appearance of weak and sharp bands at 424, 432, 420 and 426 cm^{-1}, attributed to ν(M—N), respectively, in (IV), (V), (IX), and (X) amine complexes[17]. The characteristic weak bands at 2928 and 2848 cm^{-1}; 2928 and 2848 cm^{-1}; 2924 and 2850 cm^{-1}; 2924 and 2850 cm^{-1} were assigned to the $—CH_2$ group (aliphatic) asymmetric and symmetric stretching vibrations, respectively in (IV), (V), (IX), (X) complexes. Presence of these $—CH_2$ group vibrations only in amine complexes is expected due to methylene groups of the coordinated amine molecules

In the complexes, (I)–(X) a strong and broad band in the region 1620–1610 cm^{-1} is due to conjugation in amide, which lowers >C═O frequency and coupling of >C═O and skeletal vibrations. Many weak peaks, given in Table-2, may be associated with the skeletal vibrations of the whole complex molecule in all the complexes.

Infrared spectra of organometallic compounds: An indicative evidence for the support of the structures has been noted by the new strong and sharp peaks appearing at 410, 418 and 418 cm^{-1}, respectively, in Zn^{2+}, Cu^{2+} and Ni^{2+} compounds, assigned to metal-carbon bond (ν(M—C), ligand). The other evidence of bonding of the ligand through oxygen donor to the metal ion is obtained tentatively by the appearance of sharp and weak bands at 450, 460, 458 cm^{-1} (ν(M—O), ligand)[11] in the far IR spectra of the Zn^{2+}, Cu^{2+} and Ni^{2+} compounds, respectively. The weak and sharp bands are related to >C═O group appearing at 1680, 1700 and 1682 cm^{-1} frequencies in the Zn^{2+}, Cu^{2+} and Ni^{2+} compounds, respectively. In the infrared spectra of Zn^{2+} compound, a weak band due to association of dimethylformamide appears at 1620 cm^{-1} owing to the reasons described earlier for compounds (I)–(X). Due to the absence of DMF in compunds (XI) and (XII) the corresponding band disappears. But, the presence of coordinated water is indicated in these compounds by the appearance of bands at 3477, 3470 and 3395, 3390 cm^{-1} followed by the other peaks at 1650, 1650 cm^{-1}; 755, 760 cm^{-1}; 692, 696 cm^{-1}; assigned to the O—H asymmetric and symmetric stretching, deformation; rocking, wagging vibrations[12, 14], respectively. The complexes of Cu^{2+} and Ni^{2+} also show bands at 628 and 624 cm^{-1} respectively, which may be assigned to ν(M—O)(H_2O) vibrations[13, 14]

The characteristic sharp bands, C—H stretching and scissoring appear at 2944, 2942 cm^{-1} and 1453, 1450 cm^{-1}, respectively in compounds (XI) and (XII). The other peaks appearing in the region 1600–1450 cm^{-1} (XII, XIII) and 1212–1012 cm^{-1} (XI–XIII) may be due to the skeletal vibrations in plane and skeletal vibrations of the whole complex molecule, respectively.

The molar conductivities of the compounds (Table-1) are in support of ionic and non-ionic nature of the complexes (II), (III), (V), (VII), (VIII), (X) and (I), (IV), (VI), (IX), respectively.

TABLE-2

THE IMPORTANT IR BANDS (cm^{-1}) OF THE PHTHALIC ACID COMPLEXES

Compound	IR bands (cm^{-1})
$CuL\cdot 2H_2O\cdot 2DMF$ (I)	3456 (m, b), 3104 (m, sp), 1612 (s, b), 1488 (s, sp), 1404 (s, b), 1148 (s, vsp), 1100 (m, vsp), 1052 (vw, sh), 880 (m, sp), 842 (m, vsp), 770 (s, sp), 706 (s, sp), 528 (m, sp), 472 (m, sp), 658 (m, vsp).
$Na_2[CuL_2\cdot 2H_2O]\cdot DMF$ (II)	3456 (m, sp), 3104 (s, b), 1580 (s, b), 1484 (s, sp), 1388 (s, b), 1148 (s, vsp), 1100 (s, vsp), 1070 (m, sp), 870 (m, sp), 842 (m, sp), 776 (m, sp), 746 (s, sp), 654 (s, vsp), 576 (m, sp), 504 (m, sp), 456 (m, sp).
$Na_4[CuL_3]\cdot 5DMF$ (III)	1612 (s, b), 1484 (s, sp), 1398 (s, b), 1148 (s, vsp), 1090 (s, vsp), 870 (s, vsp), 838 (s, vsp), 802 (s, vsp), 722 (s, sp), 706 (s, sp), 576 (m, sp), 496 (s, b).
$[CuL\cdot 2DP]\cdot 2DMF$ (IV)	3312 (s, sp), 3264 (s, sp), 2928 (w, sp), 2848 (w), 1620 (s, b), 1580 (s, b), 1388 (s, sp), 1356 (sh), 1260 (w, vsp), 1180 (w, vsp), 970 (w, vsp), 850 (m, vsp), 744 (m, vsp), 698 (m, vsp), 504 (w, sp), 472 (w, sp), 424 (w, sp).
$Na_2[CuL_2\cdot DP]\cdot 5DMF$ (V)	3312 (s, b), 3200 (w), 2928 (w, sp). 2848 (vw), 1612 (w, sh), 1564 (vs, sp), 1404 (s, sp), 1388 (sh), 1180 (m, sp), 1090(w, vsp), 1060 (m, sp), 930 (w, sp), 834 (w, b), 760 (m, sp), 690 (w, sp), 504 (w, sp), 488 (w, sp), 432 (w, sp).
$[NiL\cdot 2H_2O\cdot 2DMF]$ (VI)	3460 (m, b), 3100 (m), 1615 (s, b), 1482 (s, sp), 1396 (s, b), 1140 (s, vsp), 1100 (m, vsp), 874 (m), 852 (m, vsp), 780 (s, sp), 700 (s, sp), 646 (m, sp), 526 (m, sp), 460 (m, sp).
$Na_2[NiL_2\cdot 2DMF]$ (VII)	3100 (m), 1612 (s, b), 1480 (s, sp), 1390 (s, b) 1146 (s, vsp), 1098 (s, vsp), 870 (w, sp), 830 (m), 780 (m, sp), 700 (m), 572 (m), 530 (w), 510 (vw), 450 (m, sp).
$Na_4[NiL_3]\cdot 3.5DMF$ (VIII)	1600 (s, b), 1486 (s, sp), 1398 (s, b), 1142 (s, vsp), 1092 (s, sp), 870 (m, sp), 826 (s, sp), 760 (m, sp), 680 (m, sp), 572 (m), 540 (m, sp), 480 (s, b).
$[NiL\cdot 2DP]\cdot 0.5DMF$ (IX)	3324 (s, sp), 3280 (s, sp), 2924 (w), 2850 (w), 1616 (s, b), 1580 (s, b), 1386 (s, sp), 1255 (w, sp), 965 (m, sp), 850 (w, sp), 740 (m), 694 (m, vsp), 508 (w), 468 (w, sp), 420 (w, sp).
$Na_2[NiL_2\cdot DP]\cdot DMF$ (X)	3328 (s), 3216 (s), 2924 (w), 2850 (vw, sp), 1600 (s, b), 1584 (s, sp), 1396 (s, sp), 1170 (m, sp), 1086 (w), 928 (w, sp), 830 (w, vsp), 758 (m, sp), 694 (m, sp), 508 (w), 480 (w, sp), 426 (w, sp).
$Cu(C_7H_4O_2)(2H_2O)$ (XI)	3477 (w, sp), 3395 (s, sp), 2944 (vw, sp), 1700 (w, sp), 1650 (w, sp), 1643 (w, sp), 1600 (s, sp), 1540 (s, sp), 1453 (w, sp), 1210 (sp), 1162 (vw, b), 1012 (vw, sp), 755 (m, sp), 692 (vw, b), 628 (s, b), 472 (m, sp), 460 (w, sp), 418 (vs, vsp).
$Ni(C_7H_4O_2)(2H_2O)$ (XII)	3470 (vw), 3390 (s), 2942 (vw, sp), 1682 (w, sp), 1650 (w, sp), 1640 (w, sp), 1600 (s, sp), 1538 (s, sp), 1450 (w), 1212 (w, sp), 1160 (w, sp), 1120 (w), 1012 (w, sp), 760 (m, sp), 696 (w), 624 (m, sp), 474 (vw), 458 (w, sp), 418 (vs, sp).
$Zn(C_7H_4O_2)(DMF)$ (XIII)	1680 (w, sp), 1620 (w), 1490 (s, sp), 1398 (s, b), 1150 (s, sp), 1090 (m, sp), 1048 (w), 884 (m, sp), 790 (s), 540 (m, sp), 450 (m, sp), 410 (s, sp).

Abbreviations used: b–broad, m–medium, s–strong, sp–sharp, sh–shoulder, vs–very strong, vsp–very sharp, vw–very weak, w–weak.

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