

Preparation and Characterization of 2,2'-Dipyridylamine, 2,2'-Dipyridylketone and 2,2'-Dithiodipyridine Complexes of Cu(II), Zn(II), Ni(II) and U(VI) Metal Ions⁺

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Summary: The neutral ligand (L) [where L = 2,2'-dipyridylamine (dpa), 2,2'-dipyridylketone (dpk) and 2,2'-dithiodipyridine (dtdp)] acts as bidentate electron donor to the metal. A methanolic solution of the metal salt $MX_2 \cdot nH_2O$ [where M = Cu(II), Zn(II), Ni(II) and UO₂(VI) and X = Cl, Br] reacts with the ligand (L) in (1:1) mole ratio to give complex of the type $[ML X_2]$ in association with or without the solvent molecule. However the salt Cu(II) when treated with (dpa) in (1:2) it yields the complex $[Cu(dpa)_2]X_2$ and with the ligand (dtdp) it yields only one type of the complex $[Cu(dtdp) X_2]$ even when a large excess of the ligand is used. All the complexes were characterized by their infrared spectra and elemental analyses. On the basis of infrared spectra it has been suggested that the ligands coordinate to the metal through the pyridine-N atoms. However the ligand (dpk) showed a low $\nu_{C=O}$ stretching frequency indicating a direct interaction between the metal and the keto group of the ligand.

Introduction

Transition metals in low oxidation states are known to coordinate with neutral electron donor ligands to give stable complexes [1- 3]. The knowledge on the mode of coordination of such ligands with transition metal ions in different oxidation states is well documented [4-6]. The ligand (dpa) is known to react with Cu(II) salt [5], while our work was in progress, the first ever known complex of Cu(I) halides of (dpa) as a dimer of the type $[(dpa)Cu I_2 Cu(dpa)]$ was reported alongwith its x-ray structure [7]. The bidentate nature of the ligand (dpa) has also been shown in Mo(CO)₄ (dpa) complex [8]. We have prepared and studied the complexes of Cu(II), Zn(II), Ni(II) and UO₂ X₂(VI) with ligands (dpa), (dpk) and (dtdp). Since most of the Cu(II) complexes of (dpa) and (dpk) are green or blue, it is therefore suggested that they are tetragonally distorted [9]. All these ligands act as bidentate and coordination to the metal occurs through the pyridine-N atoms. The IR spectra of all the complexes are given in Table 2 and the elemental analyses in Table 1. All the complexes are coloured, crystallised solids and very stable in the air. They are insoluble in petroleum ether, benzene and chloroform but slightly soluble in ethanol on acetone.

Results and Discussion

The methanolic solution of all the metal salts react readily with ligand (dpa), (dpk) and (dtdp) in (1:1) mole ratio giving very stable crystalline solids of the general formula $[M(II) L X_2]$ with or without solvent molecule associated with the complex. The Cu(II) salt also reacts with the ligand (dpa) in (1:2) ratio giving $[Cu(dpa)_2]X_2$ complex and so does the Ni(II) salt with (dpk) ligand. However when Zn(II) salt was treated with large excess of the ligand (dpa) or (dpk) only one type of complex (Zn L X₂) CH₃ OH was formed. (See Table 1 for details).

The study of IR spectra of Cu(II) complexes of (dpa) with (1:1) or (1:2) mole ratio as found in complexes (1-4) show an increase of (*ca.* 45 cm⁻¹) and (*ca.* 85 cm⁻¹) corresponding to (asym) and (sym) ν_{NH} stretching frequencies. Also there is an increase of (*ca.* 35 cm⁻¹) in the ν_{NH} in these complexes which indicates that the ligand (dpa) coordinates to the metal Cu(II) through the pyridine-N atoms and not through the amino group of the ligand as shown in Fig. (A).

However the IR spectra of Cu(II) and Zn(II) complexes of (dpk) show a decrease of (*ca.* 75 cm⁻¹) in the stretching frequencies of the keto

⁺ Dedicated to Dr. M.Tufail on his 60th birthday.

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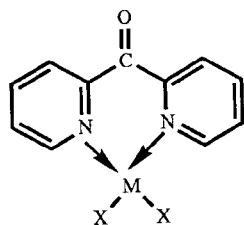


FIG. (A)

group compared with the free ligand (See Table 2). This decrease suggests that there is a direct interaction between the keto group of the (dpk) ligand and the metal, while the Ni(II) complexes (1) and (11) show an increase in the $\nu_{C=O}$ group which indicates that there is no direct interaction between the keto group and the metal.

It is noteworthy that the reaction between the ligand (dt dp) and Cu(II) or Zn(II) salts in (1:1) or even with a large excess of the ligand yields only one type of complexes $[M(II) (dt dp) X_2]$.

The elemental analyses of all the complexes are consistent with the proposed formulation as shown in Table 1.

Experimental

Materials

The ligands 2,2'-dipyridylamine, 2,2'-dipyridylketone and 2,2'-dithiodipyridine and $CuCl_2 \cdot 2H_2O$, $CuBr_2$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2 \cdot xH_2O$ were purchased from Fluka Inc. and $UO_2Cl_2 \cdot 2H_2O$ was purchased from BDH Chemical Ltd, U.K. Methanol was dried by standard procedure.

Physical measurements

All the IR spectra were measured as KBr pellets using Pye. Unicam Spectrophotometer Model SP 1320. Elemental analyses were carried out by the Microanalytical Laboratory of King Abdulaziz University, Jeddah.

Preparation of compounds

Preparation of 2,2'-dipyridylketone Copper(II) dibromide

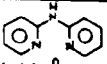
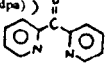
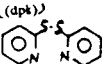
A typical method is described. Methanolic solutions of $CuBr_2$ (1.0 g; 4.4 mmol) and the ligand 2,2'-dipyridylketone (0.82 g; 4.4 mmol) were mixed.

Table 1: Analytical Data (%)^a

No.	Compound	C	H	N	Colour
1	$Cu(dpa)Br_2$ (1:1)	30.3 (30.4)	2.2 (2.2)	10.5 (10.6)	Light green
2	$[Cu(dpa)_2]Br_2$ (1:2)	41.9 (42.2)	3.6 (3.8)	14.4 (14.8)	Light green
3	$Cu(dpa)Cl_2^4$ (1:1)	40.2 (30.9)	2.9 (2.9)	3.8 (13.7)	Light green
4	$[Cu(dpa)_2]Cl_2^4$ (1:2)	50.1 (50.3)	3.7 (3.8)	17.5 (17.6)	Bright green
5	$UO_2Cl_2 \cdot dpa$ (1:1)	22.2 (23.4)	1.8 (1.7)	8.1 (8.2)	Yellow
6	$ZnCl_2 \cdot dpa \cdot CH_3OH$ (1:1) or excess	38.9 (38.9)	3.1 (3.8)	10.5 (10.3)	Colourless
7	$CuCl_2 \cdot dpk \cdot CH_3OH$ (1:1) or excess	40.8 (41.0)	3.4 (3.4)	7.9 (7.9)	Blue green
8	$CuBr_2 \cdot dpk \cdot CH_3OH$ (1:1) or excess	32.8 (32.8)	2.8 (2.7)	6.7 (6.4)	Light green
9	$ZnCl_2 \cdot dpk \cdot CH_2OH$ (1:1) or excess	41.2 (40.9)	3.6 (3.4)	7.2 (7.9)	Colourless
10	$NiCl_2 \cdot dpk \cdot CH_3OH$ (1:1)	41.3 (41.6)	3.3 (3.5)	8.3 (8.1)	Light blue
11	$[Ni(dpk)_2]Cl_2 \cdot CH_3OH$ (1:2)	51.8 (52.1)	3.7 (3.8)	10.6 (10.6)	Violet blue
12	$Cu(dtph)Cl_2$ (1:1) or excess	33.6 (33.8)	2.3 (2.2)	8.0 (7.9)	Reddish brown
13	$Cu(dt dp)Br_2$ (1:1) or excess	26.8 (27.0)	1.9 (1.8)	6.5 (6.3)	Brown

(a) The calculated values are in the parentheses.

Table 2: Infrared spectra (in cm^{-1})^(a)

Complex	$\nu_{\text{N-H}}$ (asym) and (sym)	δ_{NH} or or $\nu_{\text{C=O}}$	Other bands
Free 	3245, 3165, 3090	1580	1555, 1518, 1470, 1450, 1425, 1330, 1300, 1140, 984, 905, 756, 725.
Free 		1665	1570, 1460, 1420, 1310, 1270, 1220, 1140, 1080, 1040, 985, 930, 820, 775, 730, 690
Free 			1560, 1437, 1440, 1270, 1140, 1106, 1078, 1038, 980, 745.
1 Cu(dpa) Br ₂ (1:1)	3290, 3230	1622	1575, 1511, 1462, 1424, 1220, 1150, 1010, 760.
2 [Cu(dpa) ₂] Br ₂ (1:2)	3280, 3160, 3040	1625	1575, 1515, 1465, 1420, 1362, 1227, 1148, 1010, 845, 762.
3 Cu(dpa) Cl ₂	3290, 3230	1622	1575, 1515, 1465, 1425, 1222, 1150, 1010, 765.
4 [Cu(dpa) ₂] Cl ₂ (1:2)	3275, 3170	1627	1572, 151, 1465, 1420, 1360, 1260, 1230, 1150, 1005, 900, 760.
5 UO ₂ Cl ₂ dpa	3270, 3140	1652	3300, V.b., 1600, 1556, 1450, 1240, 1150, 1000, 910, 763.
6 Zn(dpa)Cl ₂ .CH ₃ OH	3295, 3195,	1625	1575, 1470, 1415, 3140 1375, 1265, 1225 1150, 1015, 900, 860, 750.
7 Cu(dpk)Cl ₂ .CH ₃ OH	-	1600	3150, V.b., 1435, 1295, 1205, 1158, 1085, 1010, 925, 900, 795, 755.
8 Cu(dpk) Br ₂ .CH ₃ OH	-	1595	3230, V.b., 1436, 1300, 1265, 1240, 1145, 1085, 1042, 790, 755.
9 Zn(dpk) Cl ₂ .CH ₃ OH	-	1600	3300, V.b., 1460, 1435, 1350, 1300, 1285, 1265, 1230, 1185, 1150, 1135, 1075, 1020, 935, 760.
10 Ni(dpk)Cl ₂ .CH ₃ OH	-	1675	3400, V.b., 1435, 1305, 1275, 1230, 1160, 1085, 1015, 985, 1015, 935, 295, 750.
11 [Ni(dpk) ₂]Cl ₂ .CH ₃ OH	-	1686	3300, V.b., 1600, 1450, 1320, 1290, 1245, 1180, 1030, 1005, 950, 815, 765.
12 Cu(dt dp) Cl ₂	-	-	1575, 1546, 1445, 1410, 1275, 1145, 1115, 1060, 1046, 1018, 760.
13 Cu(dt dp) Br ₂	-	-	1570, 1440, 1410, 1265, 1235, 1150, 1040, 1016, 765.

(a) KBr pellets

The mixture was stirred for 1 h at room temperature. The bulk of the solution was reduced and left the solution over night. Light green crystals were formed. These were filtered and washed first with small amount of methanol and then with diethyl ether. These crystals were dried under vacuum. All the preparations were carried out using the same procedure with the required stoichiometry of the ligands and the metal salts in methanol.

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