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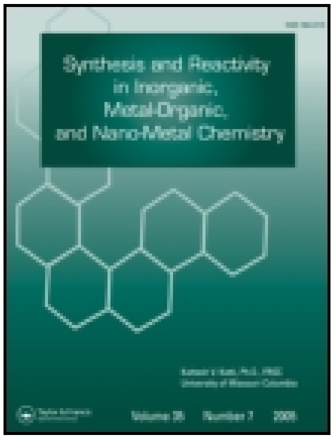

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SYNTHESIS AND CHARACTERIZATION OF NICKEL(II), ZINC(II), AND CADMIUM(II) MIXED-LIGAND COMPLEXES WITH 2,2′-BIPYRIDYLAMINE AND PHENOLS

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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SYNTHESIS AND CHARACTERIZATION OF NICKEL(II), ZINC(II), AND CADMIUM(II) MIXED-LIGAND COMPLEXES WITH 2,2′-BIPYRIDYLAMINE AND PHENOLS

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ABSTRACT

The present investigation reports the synthesis of mixed-ligand complexes of the type MAL, where M = Ni(II), Zn(II), Cd(II) A = 2,2′-bipyridylamine and H_2L^1 = catechol, H_2L^2 = pyrogallol, H_2L^3 = 2,3-dihydroxynaphthalene, H_2L^4 = protocatechuic acid. Their structures have been elucidated on the basis of elemental analyses, conductivity, thermogravimetric, magnetic moments and IR spectroscopy. The results are in accord with an octahedral environment around the central metal ions except for Ni(II). All chelates are diamagnetic. A study of the thermal properties has also been carried out.

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INTRODUCTION

An extensive review of the literature reveals that mixed-ligand complexes serve as suitable models for valuable information in the elucidation of enzymatic processes of biological relevance.[1–4] The presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation, storage and transport of transition metals in living organisms.[5–7] Antimicrobial activities of Ni(II), Zn(II), Cd(II) ions have been reported.[8–9] The activity of nickel is known because it is a component of a hydrolase[10] (urease) and it activates the genes of hydrogenases.[11] Zinc participitates in many hydrolytic reactions and in the control of gene activity by proteins with fingers.[12] Transition metals play a key role in biological systems such as cell division, respiration, nitrogen fixation and photosynthesis.[13] This biological importance has encouraged us to synthesize and study new heterochelates of Ni(II), Zn(II), Cd(II). These complexes are also good bactericides and fungicides.[14]

In the current communication are reported, the heterochelates of Ni(II), Zn(II), Cd(II) with 2,2′-bipyridylamine and phenols such as catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid.

EXPERIMENTAL

Materials

The phenols were of BDH Analar grade. The primary ligand 2,2′-bipyridylamine was obtained from Fluka. Stock solutions of Ni(II), Zn(II), and Cd(II) perchlorates were prepared and standardized by complexometic methods.[15]

Preparation of Complexes

The synthesis of the complexes was carried out by mixing 10 mL of a 0.1 M aqueous solutions of Ni(II), Zn(II), or Cd(II) perchlorates with 10 mL of a 0.1 M solution of 2,2′-bipyridylamine in ethanol. After stirring this mixture for 5–7 min, 10 mL of a 0.1 M solution of the phenol in ethanol was added slowly with constant stirring. There was no immediate precipitation. The pH of the above solutions was then raised to ~7.0 using 0.1 M sodium hydroxide solution which resulted in the precipitation of solids. The complexes thus obtained were washed well with a 1:1 mixture of absolute alcohol and water to remove unreacted metal salt and ligand. All complexes were dried at room temperature at 27 °C and kept in a vacuum desiccator.

Analyses and Physical Measurements

Elemental analyses were performed with a Coleman C, H, N analyzer. The metal content was determined[16] by titration with a solution of standardized disodium salt of EDTA after decomposing the complexes with a mixture of concentrated hydrochloric acid, nitric acid, perchloric acid and sulfuric acid in 5:2:3:2 mL ratio, respectively. Magnetic susceptibilities were measured by the Gouy method[17] at room temperature using $Hg[Co(CNS)_4]$ as calibrant. The IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer in KBr pellets. The UV-Visible reflectance spectra were measured on a Beckman DK-2A spectrophotometer using MgO as reference. Thermal measurements were performed using a Du Pont thermal analyser at a 10 $^\circ C\,min^{-1}$ heating rate.

RESULTS AND DISCUSSION

The analytical data of the complexes presented in Table I indicate 1:1:1 stoichiometry. The general equation for the formation of the complex with catechol is shown as below.

$$M^{2+} + A + H_2L \rightarrow [MAL] + 2H^+$$

$$L = L^1, L^2, L^3 \text{ and } L^4$$

All of the chelates possess high decomposition points and are colored, except the [Zn(A)(protocatechuic acid)] complex which is white. All are amorphous and stable in air. The chelates are partially soluble in ethanol and insoluble in water and other organic solvents. Hence, it was not possible to characterize them by conventional methods like osmometry or viscosity measurements.

Conductance Measurements

The complexes were found to be partially soluble in alcohol and insoluble in water and other organic solvent. The conductivity of

Table I. Analytical Data and Some Physical Properties of the Metal Complexes[a]

Compound	Molar Conductance $\Lambda m\ ohm^{-1}\ cm^{2}\ mol^{-1}$	Color	Formula Weight	Yield % (g)	Analysis (%) Found (Calculated)				D.p.[b] °C
					M	C	H	N	
$[NiAL^1]\cdot H_2O$ $C_{16}H_{15}N_3NiO_3$	11	Black	356	52 (4.58)	16.35 (16.49)	53.85 (53.93)	4.15 (4.21)	11.60 (11.79)	>300
$[NiAL^2]\cdot H_2O$ $C_{16}H_{15}N_3NiO_4$	14	Light Brown	372	62 (5.72)	15.59 (15.79)	51.65 (51.61)	4.00 (4.03)	11.23 (11.29)	>300
$[NiAL^3]\cdot H_2O$ $C_{20}H_{17}N_3NiO_3$	15	Grey	406	57 (5.64)	14.34 (14.46)	59.09 (59.11)	4.25 (4.18)	10.29 (10.34)	>300
$[NiAL^4]\cdot H_2O$ $C_{17}H_{15}N_3NiO_4$	17	Yellowish Brown	384	55 (5.25)	15.60 (15.28)	53.20 (53.12)	3.93 (3.90)	11.0 (10.93)	>300
$[ZnAL^1]\cdot H_2O$ $C_{16}H_{15}N_3O_3Zn$	16	Grey	362.7	62 (5.62)	17.93 (18.06)	53.10 (53.03)	4.09 (4.14)	11.35 (11.06)	>350
$[ZnAL^2]\cdot H_2O$ $C_{16}H_{15}N_3O_4Zn$	19	Yellowish Brown	378.7	60 (5.68)	17.09 (17.29)	50.50 (50.79)	3.90 (3.96)	11.03 (11.11)	>350

[ZnAL^3]·H_2O	20	Light Pinkish	412.7	63	15.76	58.06	4.09	10.06	>350
$C_{20}H_{17}N_3O_3Zn$				(6.50)	(15.86)	(58.25)	(4.12)	(10.19)	
[ZnAL^4]·H_2O	21	Dirty White	406.7	59	16.86	52.35	3.72	10.37	>350
$C_{17}H_{15}N_3O_5Zn$				(6.00)	(16.76)	(52.10)	(3.84)	(10.76)	
[CdAL^1]·H_2O	16	Light Grey	409.7	70	27.08	46.12	3.80	10.43	>280
$C_{16}H_{15}CdN_3O_3$				(7.17)	(27.38)	(46.94)	(3.67)	(10.27)	
[CdAL^2]·H_2O	19	Dark Brown	425.7	65	26.10	44.94	3.24	10.01	>275
$C_{16}H_{15}CdN_3O_4$				(6.92)	(26.37)	(45.18)	(3.53)	(9.98)	
[CdAL^3]·H_2O	21	Light Pinkish White	459.8	72	24.10	52.70	3.61	9.96	>300
$C_{20}H_{17}CdN_3O_3$				(8.28)	(24.40)	(52.28)	(3.70)	(9.15)	
[CdAL^4]·H_2O	23	Light Yellowish Brown	453.7	67	24.36	44.94	3.03	9.05	>285
$C_{17}H_{15}CdN_3O_5$				(7.60)	(24.72)	(45.05)	(3.31)	(9.27)	

[a] A = 2,2′-bipyridylamine; L^1 = catechol dianion; L^2 = pyrogallol dianion; L^3 = 2,3-dihydroxynaphthalene dianion; L^4 = protocatechuic acid dianion; [b] decomposition point.

the alcoholic solution was measured using a Toshniwal conductivity bridge. The complexes were found to be non-electrolytes. The molar conductance values of the complexes are listed in Table 1.

Infrared Spectra

The IR spectra also indicate the presence of 2,2′-bipyridylamine and a secondary ligand in the ternary complexes. It is known[18] that in the IR spectra of 2,2′-bipyridylamine and phenol complexes there is strong coupling between various vibrational modes of the resulting chelating rings, so quantitative interpretation of bands in the IR spectra is not possible without normal coordinate analysis. Important IR frequencies of the complexes are listed in Table II, along with their suggested assignments.

The IR spectra of all of the complexes differed from those of the ligands. The phenols showed a broad band at $2750\,\mathrm{cm}^{-1}$ due to intermolecular hydrogen bonding involving the hydrogen of the phenol.[19] This band is absent in the complexes suggesting the replacement of the hydrogen of the phenol groups by metal ion. The ν(C=N) band of 2,2′-bipyridylamine appears at $1590\,\mathrm{cm}^{-1}$. This band shifts to higher energy by $40–45\,\mathrm{cm}^{-1}$ in the metal chelates indicating the bidentate N–N coordination of a homocyclic ligand.[20] The frequency in the range $1150–1170\,\mathrm{cm}^{-1}$ is attributed to ν(C=N) stretching.[21] The presence of coordinated water in the complexes is indicated by a sharp band around $3460\,\mathrm{cm}^{-1}$ and bands at 690, 680, $920\,\mathrm{cm}^{-1}$ assigned to M–OH_2 bonds.[22] The strong ν(C–O) band at $1220–1230\,\mathrm{cm}^{-1}$ in phenol appears at $1228–1240\,\mathrm{cm}^{-1}$ in the complexes, thus showing a shift to higher frequency by $8–10\,\mathrm{cm}^{-1}$. This effect is convincing proof of coordination of the metal with the secondary ligands in all the of these complexes.[23–24] The complexes also show some new bands at $460–420\,\mathrm{cm}^{-1}$ and $580–560\,\mathrm{cm}^{-1}$ which may be assigned to ν(M–O) and ν(M–O–C), respectively.[25] The bands at $780\,\mathrm{cm}^{-1}$ and $640\,\mathrm{cm}^{-1}$ in the complexes correspond to M–N stretehing.[26]

Thermogravimetric Analysis

Thermogravimetric analyses of the 2,2′-bipyridylamine, phenols and metal chelates were carried out in air by heating at a constant rate of 10 °C per minute using a Du Pont thermoanalyzer. Under the conditions employed in these analyses, the complexes lost weight gradually during every phase of the experiment, then the samples underwent an accelerated weight loss and, finally, in the temperature range of about 500–600 °C the

Table II. Infrared Spectra of the Metal Complexes (cm^{-1})[a]

Compound	ν(N–H)	ν(O–H)	ν(C–H)	ν(C=C)	ν(C=N)	ν(M–N)	ν(M–O)
A	3420 b	–	3050 b	1600 s 1570 m	1670 m	–	–
$[NiAL^1]\cdot H_2O$	3420 b	3400 b	3050 b	1600 s 1560 m 1520 m	1650 m 1630 m	780 s	430 s
$[NiAL^2]\cdot H_2O$	3420 b	3400 b	3050 b	1580 s 1520 s	1640 m	780 s 750 s	430 s
$[NiAL^3]\cdot H_2O$	3420 b	3400 b	3050 b	1590 s 1530 m	1640 m	780 s 750 s	440 s
$[NiAL^4]\cdot H_2O$	3420 b	3400 b	3050 b	1590 s 1530 m	1640 m	780 s 750 s	440 s
$[ZnAL^1]\cdot H_2O$	3420 b	3450 b	3050 b	1600 m 1570 s	1670 m	760 s	430 m
$[ZnAL^2]\cdot H_2O$	3420 b	3400 b	3050 b	1600 s 1570 m	1670 m	770 s	430 w
$[ZnAL^3]\cdot H_2O$	3420 b	3450 b	3050 w	1600 m 1550 s	1650 m	760 s	470 m
$[ZnAL^4]\cdot H_2O$	3420 b	3400 b	3050 w	1600 s 1580 m	1670 m	760 s	450 w
$[CdAL^1]\cdot H_2O$	3420 b	3400 b	3200 b	1580 s	1650 m	760 s	420 m
$[CdAL^2]\cdot H_2O$	3420 b	3400 b	3200 b	1580 w 1620 s	1650 m	640 s	420 m
$[CdAL^3]\cdot H_2O$	3420 b	3400 b	3200 m	1580 w 1620 s	1640 m	640 s	480 m
$[CdAL^4]\cdot H_2O$	3420 b	3400 b	3200 m	1580 w 1620 s	1640 s	640 s	480 m

[a] b = broad, m = medium, s = strong, w = weak, A = 2,2′-bipyridylamine; L^1 = catechol dianion; L^2 = pyrogallol dianion; L^3 = 2,3-dihydroxynapthalene dianion; L^4 = protocatechuic acid dianion.

rate of weight loss became much more moderate. During the initial phase the gradual weight loss is due to water. In general, the water of hydration may be considered either as crystal or coordinated water. According to Nikolaev *et al.*[27] water eliminating below 150 °C can be considered as crystal water and water eliminated above 150 °C may be due to coordination to the metal ion. The nature of the water observed in the complexes is water of crystallization, as reported in our previous publications.[28]

Thermogravimetric data of the primary ligand 2,2′-bipyridylamine and the metal chelates are presented in Table III. The cumulative weight losses

Table III. Cumulative % Weight Loss Data of the Ligand and Its Metal Chelates at Various Temperatures (°C)

Compound[a]	100	150	200	250	300	350	400	450	500	550	600 °C
A	3.0	16.0	88.0	91.0	92.0	94.0	95.0	95.0	95.0	95.0	95.0
$[NiAL^1]\cdot H_2O$	9.0	11.0	14.0	51.0	79.0	81.0	89.0	90.0	90.0	91.0	91.0
$[NiAL^2]\cdot H_2O$	11.3	13.3	51.5	61.4	67.1	77.1	84.9	86.5	87.0	87.0	87.0
$[NiAL^3]\cdot H_2O$	8.5	12.2	15.0	49.3	81.3	83.4	90.0	91.0	91.0	92.0	92.0
$[NiAL^4]\cdot H_2O$	5.2	5.8	8.9	32.0	41.5	42.6	47.8	60.0	60.0	61.0	61.0
$[ZnAL^1]\cdot H_2O$	3.1	6.5	7.0	17.0	30.5	51.1	69.5	70.0	71.0	72.8	73.0
$[ZnAL^2]\cdot H_2O$	4.2	5.7	7.2	18.2	33.0	51.4	72.2	74.2	75.2	75.2	75.7
$[ZnAL^3]\cdot H_2O$	6.0	8.4	27.0	34.2	44.0	75.5	76.0	76.8	77.0	77.0	77.0
$[ZnAL^4]\cdot H_2O$	4.9	6.1	22.0	31.5	44.5	69.2	71.0	72.0	72.0	72.0	72.0
$[CdAL^1]\cdot H_2O$	1.0	1.0	1.0	12.0	36.0	43.0	46.0	48.0	50.0	62.0	71.0
$[CdAL^2]\cdot H_2O$	2.0	3.0	4.0	13.0	40.0	48.0	51.0	54.0	66.0	74.0	74.0
$[CdAL^3]\cdot H_2O$	3.0	5.0	27.0	30.0	35.0	42.0	46.0	49.0	62.0	70.0	71.0
$[CdAL^4]\cdot H_2O$	1.0	4.0	8.0	26.0	50.0	54.0	60.0	69.0	70.0	70.0	70.0

[a] A = 2,2′-bipyridylamine; L^1 = catechol dianion; L^2 = pyrogallol dianion; L^3 = 2,3-dihydroxynapthalene dianion; L^4 = protocatechuic acid dianion.

Table IV. Water Content at 25 °C and Cumulative Weight Loss Data of Metal Chelates at 100 °C and 150 °C

			Found			
	H_2O 25 °C		100 °C		150 °C	
Compound[a]	g	%	g	%	g	%
$[NiAL^1]\cdot H_2O$	18.00	5.06	32.04	9.0	39.16	11.0
$[NiAL^2]\cdot H_2O$	18.00	4.84	42.03	11.3	49.47	13.3
$[NiAL^3]\cdot H_2O$	18.00	4.43	34.51	8.5	49.53	12.2
$[NiAL^4]\cdot H_2O$	18.00	4.69	19.96	5.2	22.27	5.8
$[ZnAL^1]\cdot H_2O$	18.00	4.96	11.24	3.1	23.57	6.5
$[ZnAL^2]\cdot H_2O$	18.00	4.75	15.90	4.2	21.58	5.7
$[ZnAL^3]\cdot H_2O$	18.00	4.36	24.76	6.0	34.66	8.4
$[ZnAL^4]\cdot H_2O$	18.00	4.43	19.92	4.9	24.80	6.1
$[CdAL^1]\cdot H_2O$	18.00	4.39	4.09	1.0	4.09	1.0
$[CdAL^2]\cdot H_2O$	18.00	4.24	8.51	2.0	12.77	3.0
$[CdAL^3]\cdot H_2O$	18.00	3.91	13.79	3.0	22.99	5.0
$[CdAL^4]\cdot H_2O$	18.00	3.98	4.53	1.0	18.14	4.0

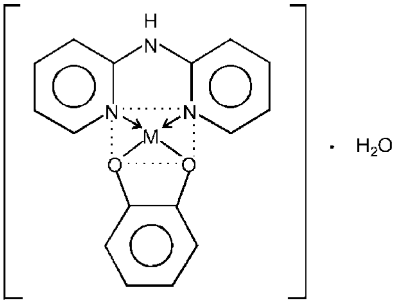
[a] A = 2,2′-bipyridylamine; L^1 = catechol dianion; L^2 = pyrogallol dianion; L^3 = 2,3-dihydroxynapthalene dianion; L^4 = protocatechuic acid dianion.

of metal chelates at 100 °C and 150 °C are presented in Table IV along with percentage of water at 25 °C. Thermogravimetric analyses indicates elimination of water and decomposition loss together. Therefore, higher percentage are observed in all the cases except $[CdAL^1]\cdot H_2O$ and $[CdAL^2]\cdot H_2O$ at 150 °C. The deviation is higher in case of Ni(II) and lower or negative in case of Cd(II) complexes and may be due to the specific nature of metal ions.

Electronic Spectra and Magnetic Measurements

The information regarding geometry of these complexes is obtained from their electronic spectral data and magnetic moments. The Ni(II) complexes were found to be diamagnetic, as expected for four-coordinated, square planar complexes.[29] The electronic spectra of the Ni(II) d^8 complexes exhibit absorptions at 15,630, 21,940 and 24,700 cm^{-1} assigned to $^1A_1 \rightarrow {}^1A_2\ (\nu_1)^1$, $^1A_1 \rightarrow {}^1B_2\ (\nu_2)$, and $^1A_1 \rightarrow {}^1E_1$ transitions[30–31] of Ni(II) in a square-planar environment due to large crystal field splitting.

The Zn(II) and Cd(II) complexes are diamagnetic as expected for d^{10} systems.[32] Bands were obtained at 28,197 cm^{-1}, 29,431 cm^{-1} (27,211),



M(II) = Cd(II), Ni(II) or Zn(II).

Figure 1. Suggested structures of the complexes shown for catechol as the phenol.

28,984 cm^{-1} and 29,449 cm^{-1} (27,344) for the Zn(II) complexes and 25,157 cm^{-1}, 28,571 cm^{-1} (24,968), 25,614 cm^{-1} and 28,571 cm^{-1} (25,477) for the Cd(II) complexes with catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid, respectively, are due to the ligands. The molar intensity (in L $mole^{-1}$ cm^{-1}) is reported in parentheses. The absence of intensity value may infer that the measurement was carried out by a different technique. Three transitions are expected, $(A_1) \rightarrow \pi^*(E)$, $(E) \rightarrow \pi^*(A_2)$ and $(E) \rightarrow \pi^*(E)$, but only one shoulder band is obtained. This band may be either due to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions of the ligands or a merger of both transitions.[33–34]

CONCLUSIONS

On the basis of elemental analyses, IR, thermogravimetric analyses, UV-Visible reflectance spectra and magnetic properties, it is possible to assign square planar to the Ni(II) and octahedral geometry to the Zn(II) and Cd(II) complexes as shown in Fig. 1. The values of β is favourable for assigned structures. The structure assignment, however, can not be considered final in the absence of x-ray crystal studies.

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