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Synthesis, Electronic and IR Spectral Studies of Some Polymeric Cobalt(II), Nickel(II), Zinc(II) and Cadmium(II) Azido Complexes with Hydrazine

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A series of polymeric cobalt(II), nickel(II), zinc(II) and cadmium(II) azido complexes with hydrazine of the type $[M(N_2H_4)(H_2O)(N_3)Cl]_n$, $[M(N_2H_4)(N_3)_2]_n$ and $[M(N_2H_4)_2(N_3)_2]_n$ have been prepared. These were characterized by elemental analyses, magnetic susceptibility measurements, electronic and IR spectra. The complexes are highly insoluble in polar and non polar solvents. All the complexes decompose with explosion at different temperatures between 100°C to 200°C. The magnetic moment and electronic spectral data for Co(II) and Ni(II) complexes suggest that the complexes have octahedral structure. The ligand-field parameters (10 Dq, B, β , β° and LFSE) have also been calculated for all Co(II) and Ni(II) complexes which indicate a significant covalent character of M-L bonds. The IR spectra of the complexes show that the azide group and hydrazine molecule both act as bidentate bridging ligands in $[M(N_2H_4)(H_2O)(N_3)Cl]_n$ and $[M(N_2H_4)(N_3)_2]_n$ type complexes but the azide group is terminally bonded to metal in all $[M(N_2H_4)_2(N_3)_2]_n$ type complexes.

Keywords: Polymeric metal(II) complexes, hydrazine, azide, electronic spectra, IR spectra

1 Introduction

The azide ion (N_3^-), having multiple bonds between nitrogen atoms (1) forms numerous coordination complexes by standard ligand replacement reactions (2). It acts as a versatile ligand which can bind metal ions in a variable manner giving rise to terminal, end-on bridging and end-to-end bridging modes (3–6). This versatility of the azide ligand enriches the stereochemistry of the transition metal ions as well as their spectroscopic and magnetic properties (7–11). The azide ligand is a good choice for the design of new polynuclear systems (12–13). The current interest in the chemistry of hydrazine complexes is not only due to their relevance in dinitrogen fixation process, but also due to their interesting reactivity and structural properties (14–17). Coordinated hydrazine NH_2NH_2 has been proposed as a possible intermediate in the nitrogen fixation process, and has been isolated by quenching the functioning enzyme nitrogenase (18).

Separately, metal hydrazides and metal azides are still being investigated, but we have taken up such a mixed hydrazide-azide system for the first time. Since both the hydrazine (N_2H_4) and azide (N_3^-) groups show monodentate and bidentate bridging character in their metal complexes, it would be interesting to study their competitive character when both are present in a single complex. Again, since metal hydrazides and metal azides tend to explode, the synthesis of mixed hydrazine-azide metal complexes would also be interesting. It is anticipated that in dilute solutions, when metal is surrounded by solvent molecules, the hydrazide-azide system could be stabilized. It is with these ideas in mind that the study has been undertaken and the results are discussed in this paper.

2 Experimental

2.1 Materials

All the chemicals used were of BDH or equivalent grade. The metal salts $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2$, $CdCl_2 \cdot H_2O$, hydrazine hydrate ($NH_2NH_2 \cdot H_2O$) and NaN_3 were obtained from S. D. Fine-Chem Limited, Mumbai (India).

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Table 1. Analytical data of the complexes

Complex (Color)	Empirical formula (Formula wt.)	Analyses found (calc)%				Yield (%)
		Metal	Cl	Azide	Hydrazine	
[Co(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n (Pink)	H ₆ N ₅ OClCo (186.5)	31.42 (31.63)	19.00 (19.03)	22.44 (22.52)	17.21 (17.16)	72
[Co(N ₂ H ₄)(N ₃) ₂] _n (Pink)	H ₄ N ₈ Co (175)	33.50 (33.71)	–	48.24 (48.00)	18.16 (18.28)	76
[Co(N ₂ H ₄) ₂ (N ₃) ₂] _n (Pink)	H ₈ N ₁₀ Co (207)	28.60 (28.50)	–	40.37 (40.58)	30.77 (30.92)	75
[Ni(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n (Light green)	H ₆ N ₅ OClNi (186.2)	31.40 (31.52)	18.92 (19.06)	22.45 (22.56)	17.06 (17.18)	70
[Ni(N ₂ H ₄)(N ₃) ₂] _n (Light green)	H ₄ N ₈ Ni (174.7)	33.45 (33.60)	–	47.90 (48.08)	18.22 (18.32)	75
[Ni(N ₂ H ₄) ₂ (N ₃) ₂] _n (Light blue)	H ₈ N ₁₀ Ni (206.7)	28.28 (28.40)	–	40.46 (40.64)	30.80 (30.96)	75
[Zn(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n (White)	H ₆ N ₅ OClZn (192.9)	33.75 (33.90)	18.32 (18.40)	21.66 (21.77)	16.50 (16.59)	80
[Zn(N ₂ H ₄)(N ₃) ₂] _n (White)	H ₄ N ₈ Zn (181.4)	35.90 (36.05)	–	46.16 (46.31)	17.52 (17.64)	76
[Zn(N ₂ H ₄) ₂ (N ₃) ₂] _n (White)	H ₈ N ₁₀ Zn (213.4)	30.51 (30.65)	–	39.23 (39.36)	29.86 (29.99)	76
[Cd(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n (White)	H ₆ N ₅ OClCd (239.9)	46.63 (46.85)	14.90 (14.80)	17.40 (17.51)	13.27 (13.34)	74
[Cd(N ₂ H ₄)(N ₃) ₂] _n (White)	H ₄ N ₈ Cd (228.4)	49.05 (49.21)	–	36.66 (36.78)	14.10 (14.01)	74
[Cd(N ₂ H ₄) ₂ (N ₃) ₂] _n (White)	H ₈ N ₁₀ Cd (260.4)	43.04 (43.16)	–	32.12 (32.26)	24.48 (24.58)	75

2.2 Synthesis of Metal Complexes

Metal(II) azido complexes with hydrazine in different compositions were synthesized by reacting 50 mL aqueous solutions containing 10 mmol each of CoCl₂·6H₂O (2.38 g), NiCl₂·6H₂O (2.37 g), ZnCl₂ (1.36 g) and CdCl₂·H₂O (2.01 g) reacting with 50 mL aqueous solutions of hydrazine hydrate (10 mmol, 0.40 mL) and sodium azide (10 mmol, 0.65 g) for the preparation of 1:1:1 (metal:hydrazine:azide) complexes; or reacting with 50 mL aqueous solutions of hydrazine hydrate (10 mmol, 0.40 mL) and sodium azide (20 mmol, 1.30 g) for the preparation of 1:1:2 metal complexes; or reacting with 50 mL aqueous solution of hydrazine hydrate (20 mmol, 0.80 mL) and sodium azide (20 mmol, 1.30 g) for the preparation of 1:2:2 metal complexes.

The above solution mixtures were stirred on a magnetic stirrer for 30 min at room temperature. The complexes were precipitated, filtered through suction and washed several times with water and finally with aqueous ethanol (50%, v/v). The compounds were dried in a desiccator over anhydrous CaCl₂ at room temperature.

2.3 Analyses of the Metal Complexes

Metal contents were determined gravimetrically by the standard literature methods (19). The chloride content was analyzed as silver chloride after decomposing the complex

with conc. HNO₃ and evaporating the residue to dryness with conc. H₂SO₄ (19). Azide was estimated as AgN₃ (20) by adding solutions of 0.1 N AgNO₃ at pH slightly below 7.0 as it dissolves in acid, as well as in basic solutions. Hydrazine content was estimated volumetrically by the literature procedure (19) by refluxing the complex with conc. HCl and titrating the solution against KIO₃ solution.

2.4 Physico-Chemical Measurements

Room temperature magnetic susceptibilities of the complexes were determined on a Faraday balance using Hg[Co(SCN)₄] as calibrant and corrected for diamagnetism (21). The electronic spectra were recorded on a Carry-14 Spectrophotometer in nujol mull. The IR spectra of the complexes were recorded on a Perkin-Elmer 621 Spectrophotometer in the range 4000–200 cm⁻¹ in nujol mull. The analytical and physico-chemical data are given in Tables 1–3.

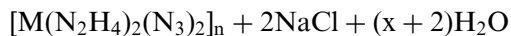
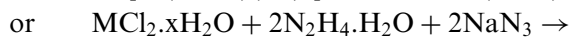
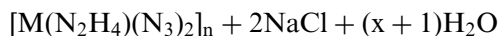
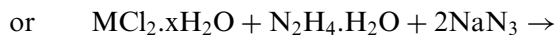
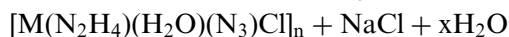
3 Results and Discussion

The analytical data (Table 1) of the metal complexes show that hydrazine hydrate (NH₂NH₂·H₂O) and sodium azide (NaN₃) react with metal(II) chlorides in 1:1:1, 1:1:2 and 1:2:2 (metal:hydrazine:azide)

Table 2. Magnetic moments, electronic spectra and ligand field parameters of the complexes

Complexes	μ_{eff} (B.M.)	Band Maxima (cm^{-1})			10 Dq (cm^{-1})	B (cm^{-1})	β	β^0 (%)	LFSE (kcal/mol)
		ν_1	ν_2	ν_3					
[Co(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n	4.93	8,500	–	19,100	10,625	848	0.873	12.7	24.22
[Co(N ₂ H ₄)(N ₃) ₂] _n	4.87	8,330	–	18,860	10,412	840	0.865	13.5	23.73
[Co(N ₂ H ₄) ₂ (N ₃) ₂] _n	5.10	8,675	–	19,260	10,844	850	0.875	12.5	24.71
[Ni(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n	3.35	10,300	16,375	27,570	10,300	870	0.836	16.4	35.21
[Ni(N ₂ H ₄)(N ₃) ₂] _n	3.23	10,600	17,450	27,770	10,600	890	0.855	14.5	36.24
[Ni(N ₂ H ₄) ₂ (N ₃) ₂] _n	3.32	10,250	16,400	27,640	10,250	886	0.851	14.9	35.04

molar ratios to give complexes of the general composition [M(N₂H₄)(H₂O)(N₃)Cl]_n, [M(N₂H₄)(N₃)₂]_n and [M(N₂H₄)₂(N₃)₂]_n. The reactions may proceed as follows:



where, M = Co(II), Ni(II), Zn(II) and Cd(II); x = 0–6

All the complexes are powdery solids. Zn(II) and Cd(II) complexes are white, Co(II) complexes are pink and Ni(II) complexes are light green to light blue in color. The complexes are insoluble in water and common organic solvents like ethanol, methanol, chloroform, carbon tetrachloride, methylene chloride, acetonitrile, benzene and nitrobenzene as well as coordinating solvents like DMSO and DMF. The non-melting nature and non solubility in common organic solvents suggest the polymeric nature of the complexes.

All the Co(II) and Ni(II) complexes explode on heating. Due to their explosive nature, our trials for observing the thermal decomposition temperature not only failed, but also damaged the apparatus. Zn(II) complexes explode with

spark and Cd(II) complexes are comparatively stable and decompose above 250°C. The explosive property of metal azide complexes depends on several factors including the nature of metal ion, its oxidation state and the nature of the complexes as a whole (6).

3.1 Magnetic Susceptibility Measurements

The room temperature magnetic susceptibility measurements show that cobalt(II) and nickel(II) complexes have μ_{eff} values corresponding to those expected from their ground state electronic configuration in a weak or medium field. Zinc(II) and cadmium(II) complexes are diamagnetic.

The magnetic moment values for octahedral, tetrahedral and square planar Co(II) complexes range from 4.7–5.2, 4.2–4.8 and 2.2–2.9 B.M., respectively (22). The μ_{eff} values of the three Co(II) hydrazine-azide complexes (4.93–5.10 B.M.) lie well within the range of the octahedral complexes (21). The magnetic moment values for high spin octahedral Ni(II) complexes are in the range of 3.0–3.5 B.M. and for tetrahedral complexes they have been observed between 3.5–4.1 B.M. This deviation may be due to the spin orbit coupling which causes an orbital contribution in the quenched ³A_{2g} ground state of Ni(II) ion in the octahedral environment and not due to the contribution of orbital

Table 3. Important IR spectral bands (cm^{-1}) and their assignments

Compounds	$\nu(\text{OH} + \text{NH})$	$\delta(\text{NH}_2)$	$\nu(\text{N-N})$	$\nu(\text{M-N})$ Azide	$\nu(\text{M-N})$ Hydrazine	Azide bands		
						$\nu_{\text{as}}(\text{N}_3)$	$\nu_{\text{s}}(\text{N}_3)$	$\delta(\text{N}_3)$
[Co(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n	3405b, 3280m, 3190m	1608s	1000w	385m	260w	2080s	1285s	585w
[Co(N ₂ H ₄)(N ₃) ₂] _n	3285b, 3180m	1605s	995w	370m	265m	2082s	1282m	580m
[Co(N ₂ H ₄) ₂ (N ₃) ₂] _n	3282b, 3176m	1601s	995w	410w	280w	2042s	1280m	620m
[Ni(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n	3410b, 3276m, 3195m	1595s	1002w	360w	250w	2090s	1290m	580w
[Ni(N ₂ H ₄)(N ₃) ₂] _n	3280b, 3188m	1598s	1003m	370m	265w	2080s	1300s	598w
[Ni(N ₂ H ₄) ₂ (N ₃) ₂] _n	3275m, 3190m	1593s	998w	400m	275w	2052s	1290m	620m
[Zn(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n	3400b, 3290b, 3192m	1605s	1005w	380w	270m	2090s	1280m	585w
[Zn(N ₂ H ₄)(N ₃) ₂] _n	3288m, 3191m	1604s	1000w	360m	275m	2092s	1300m	590w
[Zn(N ₂ H ₄) ₂ (N ₃) ₂] _n	3280b, 3190m	1600s	995m	405m	290w	2044s	1282m	635m
[Cd(N ₂ H ₄)(H ₂ O)(N ₃)Cl] _n	3390b, 3282m, 3194m	1603s	996w	375w	260w	2088s	1280s	580w
[Cd(N ₂ H ₄)(N ₃) ₂] _n	3389b, 3188m	1610s	1008w	370w	275m	2084s	1285m	585w
[Cd(N ₂ H ₄) ₂ (N ₃) ₂] _n	3281m, 3186b	1602s	1010w	420w	280m	2048s	1290m	630m

b = broad, s = strong, m = medium, w = weak

angular momentum of the electrons since the orbital momentum does not effect the $^3A_{2g}$ state (23). However, in the case of tetrahedral Ni(II) complexes, the orbital angular momentum contributes strongly to the magnetic moments leading to as high values as 4.0 B.M.. The planar complexes of Ni(II) are invariably diamagnetic or low spin type. The Ni(II) complexes reported in this paper show the μ_{eff} values 3.23–3.35 B.M. which are in accordance with the spin free octahedral geometry of the metal ions (21).

3.2 Electronic Spectra

Cobalt(II) complexes generally show three absorption bands in the visible region under the influence of the octahedral field corresponding to the transitions $^4T_{1g}$ (F) \rightarrow $^4T_{2g}$ (F) (ν_1), \rightarrow $^4A_{2g}$ (F) (ν_2) and \rightarrow $^4T_{1g}$ (P) (ν_3). In case of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, three transitions are obtained at 8,130, 17,540 and 21,980 cm^{-1} (24). In the present study, two bands have been observed at 8,500, 19,100 cm^{-1} ; 8,330, 18,860 cm^{-1} ; and 8,675, 19,260 cm^{-1} , respectively, for $[\text{Co}(\text{N}_2\text{H}_4)(\text{H}_2\text{O})(\text{N}_3)\text{Cl}]_n$, $[\text{Co}(\text{N}_2\text{H}_4)(\text{N}_3)_2]_n$ and $[\text{Co}(\text{N}_2\text{H}_4)_2(\text{N}_3)_2]_n$ suggesting an octahedral geometry around the metal ion. The ν_2 transition is not observed due to very weak intensity (25).

Nickel(II) complexes show three bands in octahedral environment corresponding to the transitions, $^3A_{2g}$ (F) \rightarrow $^3T_{2g}$ (F) (ν_1), $^3A_{2g}$ (F) \rightarrow $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) \rightarrow $^3T_{1g}$ (P) (ν_3). The above ν_1 , ν_2 and ν_3 bands for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ are observed at 8,510, 13,510 and 25,315 cm^{-1} and at 10,700, 17,540 and 28,170 cm^{-1} for $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (24). A comparison of these bands with those observed for the complexes in the present study, show octahedral stereochemistry around Ni(II) in the complexes (26). They show the bands in the region as $\nu_1 = 10,250$ – $10,600$ cm^{-1} , $\nu_2 = 16,375$ – $17,450$ cm^{-1} and $\nu_3 = 27,570$ – $27,770$ cm^{-1} . The ligand field parameters (10 Dq, B, β , β^0 and LFSE) have also been calculated for all Co(II) and Ni(II) complexes (Table 2) which indicate a significant covalent character of M-L bonds. These parameters were obtained by using the standard formula (21, 24) mentioned below:

Calculation of 10 Dq: For Ni(II) octahedral complexes: ν_1 is taken as 10 Dq;

For Co(II) octahedral complexes: $\nu_1 = 8$ Dq.

Calculation of Inter-electronic Repulsion Parameter (Racah Parameter) B:

For Ni(II) octahedral complexes: $\nu_3 + \nu_2 - 3 \nu_1 = 15$ B;

For Co(II) octahedral complexes: $\nu_3 = 6$ Dq + 15 B

Calculation of Nephelauxetic Ratio: $\beta = B/B^0$

where, B = Racah Parameter for the metal ion in the complex, B^0 = Racah Parameter for the free metal ion. ($B^0 = 971$ cm^{-1} and 1041 cm^{-1} for Co(II) and Ni(II), respectively)

% Covalency: $\beta^0 = (1 - \beta) \times 100$

Calculation of Ligand Field Stabilization Energy (LFSE):

For Co(II) octahedral complexes: LFSE = 8 Dq, For Ni(II) octahedral complexes: LFSE = 12 Dq

3.3 IR Spectra

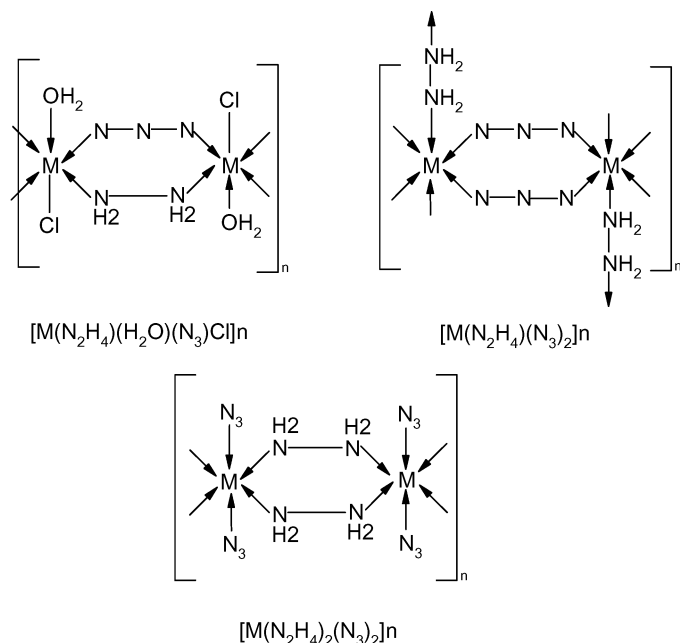
The bonding of the hydrazine ligand and azide (N_3^-) group to metal ions have been judged by a careful comparison of the infrared spectra of the complexes with those of the free ligand. A few significant bands have been selected to observe the effect on ligand vibration in the complexes.

The free azide ion shows bands at 2041, 1344 and 645 cm^{-1} which may be assigned to $\nu_{\text{as}}(\text{N}_3)$, $\nu_s(\text{N}_3)$ and $\delta(\text{N}_3)$ modes, respectively (27). The azide group in $\text{Hg}(\text{N}_3)_2$ exhibits $\nu_{\text{as}}(\text{N}_3)$ band at 2045 cm^{-1} , whereas in $\text{Hg}_2(\text{N}_3)_2$ at 2080 cm^{-1} and suggests the presence of a terminal azide group in the former and bridging azide group in the later complexes (27). Some cobalt(II) azido complexes of pyridine derivatives containing both terminal and bridging azide groups have been reported to show two $\nu_{\text{as}}(\text{N}_3)$ bands at 2044 and 2068 cm^{-1} (6).

In $[\text{M}(\text{N}_2\text{H}_4)_2(\text{N}_3)_2]_n$ complexes, the appearance of a strong intensity band in the range 2052–2042 cm^{-1} due to $\nu_{\text{as}}(\text{N}_3)$ modes, a medium to strong intensity band in the range 100–1280 cm^{-1} due to $\nu_s(\text{N}_3)$ mode and a weak to medium intensity band in the range 635–620 cm^{-1} due to $\delta(\text{N}_3)$ mode indicate that the azide groups are terminally bonded to the metal ion (6,7,13). $[\text{M}(\text{N}_2\text{H}_4)(\text{H}_2\text{O})(\text{N}_3)\text{Cl}]_n$ and $[\text{M}(\text{N}_2\text{H}_4)(\text{N}_3)_2]_n$ complexes in general, show $\nu_{\text{as}}(\text{N}_3)$ bands observed in the range 2092–2080 cm^{-1} along with $\nu_s(\text{N}_3)$ in the range 1300–1280 cm^{-1} and $\delta(\text{N}_3)$ in the range 598–580 cm^{-1} . This suggests the bridging character of azide group (6, 7, 13).

The shift in N-H stretching frequency of free gaseous hydrazine molecule from 3350 cm^{-1} to 3280 cm^{-1} in its first row transition metal complexes is mainly due to the lowering of the N-H bond order on complexation (28). The IR bands of the complexes under this study (Table 3) show two $\nu(\text{NH})$ in the ranges 3290–3275 cm^{-1} , and 3195–3176 cm^{-1} . A shift to lower wave number by 60–75 cm^{-1} in $\nu(\text{NH})$ in the complexes as compared to the free hydrazine suggests the involvement of both the $-\text{NH}_2$ groups in bonding with metal ion (26). This indicates the presence of bidentate bridging hydrazine ligands in all the metal complexes. The bands observed in the range 1610–1593 cm^{-1} can be assigned to the $-\text{NH}_2$ bending vibration (28). $\nu(\text{N-N})$ observed at 960 cm^{-1} in the free hydrazine shifts to higher frequency by 35–50 cm^{-1} in the metal complexes further indicates the coordination of both the nitrogen atoms of the hydrazine molecule (29).

A broad band observed in the region 3410–3380 cm^{-1} in all $[\text{M}(\text{N}_2\text{H}_4)(\text{H}_2\text{O})(\text{N}_3)\text{Cl}]_n$ complexes may be assigned as $\nu(\text{OH})$ indicates the presence of water molecules in these complexes (27). The above metal complexes also show weak



Where M = Co(II), Ni(II), Zn(II) and Cd(II)

Fig. 1. Structures of the metal complexes.

bands in the ranges $920\text{--}905\text{ cm}^{-1}$, $762\text{--}755\text{ cm}^{-1}$ and $651\text{--}640\text{ cm}^{-1}$ due to coordinated water (30). All the metal complexes show weak to medium intensity bands in the ranges $420\text{--}360\text{ cm}^{-1}$ may be assigned to $\nu(M\text{--}N)$ of azide-N. A different region ($290\text{--}250\text{ cm}^{-1}$) has been observed for $\nu(M\text{--}N)$ of hydrazine-N (6, 13).

In view of the above results and discussion of the observed magnetic moments, electronic and IR spectra, general structures for the metal complexes have been proposed (Figure 1).

4 Conclusions

The novel metal complexes have been synthesized for the first time in three different compositions by varying the ratios of the reactants as 1:1:1, 1:1:2 and 1:2:2 (metal: hydrazine: azide) in aqueous solution. The Co(II), Ni(II) and Zn(II) complexes explode on heating but Cd(II) complexes are stable and only decompose above 250°C . The non-melting nature and insolubility in common organic solvents of the complexes indicate that the complexes are polymeric. The Co(II) and Ni(II) complexes have a spin-free octahedral structure with significant covalent character of M-L bond. The hydrazine molecule acts as bidentate bridging ligand in all the complexes, whereas, the bonding nature of the azide group varies with the composition of the complexes. It acts as bidentate bridged in $[M(N_2H_4)(H_2O)(N_3)Cl]_n$ and $[M(N_2H_4)(N_3)_2]_n$ complexes, but terminally bonded in $[M(N_2H_4)_2(N_3)_2]_n$ complexes.

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