Indian Journal of Chemistry
Vol. 33A, September 1994, pp. 879-881

Synthesis and characterization of chromium(III), cobalt(II), manganese(II), nickel(II) and copper(II) complexes with 3-hydrazino-5,6-diphenyl-1,2,4-triazine

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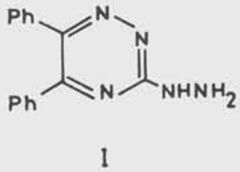
Received 8 November 1993; revised 11 February 1994; accepted 3 May 1994

The metal complexes of Cr(III), Co(II), Mn(II), Ni(II) and Cu(II) with 3-hydrazino-5,6-diphenyl-1,2,4-triazine (I), have been prepared and characterized on the basis of elemental analysis, molar conductance, magnetic moment measurements and spectral (electronic, IR) studies. In all complexes, the ligand acts as a neutral bidentate donor chelating with the metal ion through triazine nitrogen, 2, and amino nitrogen atom of hydrazine moiety. The Cu(II) and Ni(II) complexes are assigned a square planar geometry while Mn(II), Co(II) and Cr(III) complexes exhibit octahedral configuration. The ligand field parameters Dq, B′ and B of the octahedral complexes have been calculated.

The studies oriented towards exploring the complexing reactivity of triazines especially the 1,2,4-triazine derivatives, are limited[1-7]. The compound 1,2,4-triazine with pyridyl substituents in the 3 and 5-positions form stable complexes with metal ions[8-13] such as Fe(II), Co(II), Ni(II), Zn(II) and Cu(II). Owing to the stability of these complexes, the use of 1,2,4-triazine derivatives was suggested for determination of these ions as well as their application as corrosion inhibitors[11]. The substituents 6-phenyl- and 5,6-diphenyl-1,2,4-triazine can be used for the quantitative determination of thallium and palladium[14]. In this note, we report the synthesis and characterization of metal chelates of 3-hydrazino-5,6-diphenyl-1,2,4-triazine (I).



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Experimental

All the chemicals used in this study were of AR grade. The solvents used were purified according to standard procedures[15]. 3-Hydrazino-5,6-diphenyl-1,2,4-triazine was prepared[16] by heating 3-methylthio-5,6-di-phenyl-1,2,4-triazine and hydrazine hydrate for ~1 hr when yellow needle like crystals separated out. These were filtered and dried *in vacuo.*

Preparation of metal complexes

All the complexes were prepared by dissolving stoichiometric quantities of the metal chloride and chelating ligand in absolute ethanol (30 ml) at room temperature. The reaction mixture was then heated on a water bath for 30 min. The crystalline complexes formed were filtered, washed with hot water, followed by ethanol and dried *in vacuo.*

The electronic spectra of ethanolic solutions were measured at room temperature using Shimadzu UV-160A spectrophotometer. The infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer. The molar conductance of the solution ($10^{-3}M$ DMF) was measured at 25°C using a WTW LBRB conductivity bridge. A Shimadzu Torsion Magnetometer MB-100 was used for room temperature magnetic susceptibility measurements by Gouy's method[17]. The elemental analysis was performed at the Microanalysis Unit, Cairo University.

Results and discussion

The characterization data of the complexes are presented in Table 1.

Triazine complexes are soluble in most of the organic solvents. The molar conductance values indicate that copper(II) and nickel(II) complexes have 1:2 stoichiometry whereas the chromium(III) complex is formed in 1:1 ratio and all these complexes are electrolytic in nature. The cobalt(II) and manganese(II) complexes were found to be nonelectrolytic in nature.

The electronic spectra of ethanolic solution of Co(II) complex exhibit three bands at 8058, 16183 and 18050 cm^{-1} which are assigned to ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)\,\nu_1$, ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)\,\nu_2$ and ${}^4T_{1g} \leftarrow {}^4T_{1g}(F)\,\nu_3$ transitions, respectively, indicating an octahedral configuration around Co(II) ion. The octahedral geometry of the Co(II) complex is further confirmed by the value of the magnetic moment (5.1 B.M.) The calculated spectral parameters ν_2/ν_1, Dq/B, B and β (Table 2) have the

Table 1—Characterization data of triazine complexes

Complex (colour)	Found (Calc.), %				Λ_M mho cm^{2}mol^{-1}	μ_{eff} B.M.
	C	H	N	Cl		
$[CrL_2Cl_2]Cl \cdot 2H_2O$ (violet)	50.0 (49.97)	3.9 (4.2)	19.6 (19.4)	14.1 (14.71)	85.4	3.88
$[CoL_2Cl_2]$ (reddish brown)	54.4 (54.9)	4.2 (3.99)	21.0 (21.3)	10.2 (10.8)	13.9	5.12
$[MnL_2Cl_2].H_2O$ (greenish brown)	53.9 (53.7)	4.0 (4.2)	20.7 (20.9)	10.4 (10.6)	18.2	5.79
$[NiL_2]Cl_2.H_2O$ (orange)	53.3 (53.4)	4.4 (4.19)	21.0 (20.88)	10.7 (10.5)	126.3	dia.
$[CuL_2]Cl_2$ (brown)	54.8 (54.50)	4.0 (3.96)	21.6 (21.18)	10.9 (10.74)	119.5	1.82

Table 2—Electronic spectral data of octahedral triazine complexes

Complex	Assignment (cm^{-1})											
	ν_1		ν_2		ν_2/ν_1	ν_3		10Dq	B	Dq/B	β	C
	Calc.	Obs.	Calc.	Obs.		Calc.	Obs.					
$[CoL_2Cl_2]$	8094	8058	16409	16183	2.0	18378	18050	9600	768	1.22	0.79	3558
$[MnL_2Cl_2].2H_2O$	15850	15810	24130	24230	1.53	37884	37786	10870	659	1.65	0.76	3506
$[CrL_2Cl_2]Cl.2H_2O$	170.29	17140	24079	24390	1.42	37805		17140	745	2.3	0.81	3352

values 2.0, 1.25, 760 cm^{-1} and 0.79, respectively, which are in good agreement with the reported values for octahedral Co(II) complexes.

Five electronic transitions are observed at 15810, $^4T_{1g}(G) \leftarrow {}^6A_{1g}$; 19760, $^4T_{2g}(G) \leftarrow {}^6A_{1g}$; 24123, $^4A_{1g} \leftarrow {}^6A_{1g}$; 26200, $^4T_{2g}(D) \leftarrow {}^6A_{1g}$ and 28735 cm^{-1}, $^4E_g(D) \leftarrow {}^6A_{1g}$; for Mn(II) complex of 3-hydrazino, 5,6-diphenyl, 1,2,4-triazine. An intense band at 35808 cm^{-1} is assigned to charge transfer transitions. The bands are consistent with an octahedral complex of Mn(II). The spectral parameters Dq/B, B, β and C were calculated from the observed λ_{max} values of the electronic transitions and the expressions for the energies of the excited states relative to the ground state[18], $^4E_1\,{}^4A_1(G^4) = 10B + 5C$ and $^4E(^4D) = 17B + 5C$ (Table 2).

The electronic spectra of the chromium(III) complex in ethanolic solutions exhibit only two *d-d* transitions at 17140 and 24390 cm^{-1} which are assigned to the $^4T_{2g} \leftarrow {}^4A_{2g}(\nu_1)$ and $^4T_{1g}(F) \leftarrow {}^4A_{2g}(\nu_2)$ transitions, respectively. The highest band, the $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ transition (ν_3), however, is obscured by the intense band present in the ultraviolet region[18]. The predicted value of ν_3 was found to be 37805 cm^{-1}. The ligand field parameters ν_2/ν_1, Dq/B, B and β values were calculated according to Lever[18] and are given in Table 2. These values as well as the magnetic moment value (3.88 BM) support the octahedral structure of chromium(III) complex with 3-hydrazino-5,6-diphenyl, 1,2,4-triazine.

On comparing the degree of covalency of the above octahedral complexes, it is noted that the lowering in the B-value from that of the free ion of Co(II), Mn(II) and Cr(III) which are 971, 860 and 918 cm^{-1}, respectively is associated with a reduction in the nuclear charge on the cation[19], the reduction being pronounced with the more polarisable metal ion. The covalent character of triazine chelates are in the order, Mn(II) > Cr(III) > Co(II).

The electronic absorption spectra of Ni(II) complex of 3-hydrazino, 5,6-diphenyl, 1,2,4-triazine show a band at ~13375 cm^{-1} which assumes a square planar configuration around Ni(II)[20]. In addition, a charge transfer band is observed at 24096 cm^{-1} together with relatively weaker bands at 20605 and 15180 cm^{-1}. The diamagnetic behaviour of the nickel(II) complex and the molar conductance values indicate a square planar geometry of nickel(II) complex.

The electronic absorption spectra of Cu(II) complex consist of a broad band in the region 14400-14900 cm^{-1}, which is assigned to $^2A_{1g} \leftarrow {}^2B_{1g}$ transition as well as a shoulder in the range 21600-22200 cm^{-1} characteristic of a square planar geometry for copper(II) complexes. The spectrophotometric studies of different che-

Table 1—Colour, melting point and analytical data of the complexes of potassium bis(bismuthiol-I-yl)borate

Compounds (colour)	M.P. (°C) (decomp.)	Found (Calc.), %			
		C	N	S	M
$K^+(C_4N_4S_6B)^-$ (White)	210	13.80 (13.87)	16.10 (16.18)	55.30 (55.49)	—
$Cr(C_4N_4S_6B)_3$ (Grey)	230	14.81 (14.76)	17.20 (17.10)	59.06 (59.19)	5.19 (5.34)
$Mn(C_4N_4S_6B)_2$ (Brown)	215	14.18 (14.35)	16.60 (16.74)	57.20 (57.39)	8.10 (8.22)
$Fe(C_4N_4S_6B)_3$ (Dark brown)	205	14.62 (14.74)	17.14 (17.19)	58.78 (58.95)	5.61 (5.73)
$Co(C_4N_4S_6B)_2$ (Greenish yellow)	195	14.31 (14.20)	16.49 (16.64)	57.41 (57.65)	8.61 (8.76)
$Ni(C_4N_4S_6B)_2$ (Yellowish green)	200	14.21 (14.27)	16.60 (16.65)	57.00 (57.08)	8.64 (8.72)
$Cu(C_4N_4S_6B)_2$ (Light yellow)	225	14.00 (14.13)	16.41 (16.48)	56.31 (56.52)	9.43 (9.63)
$Zn(C_4N_4S_6B)_2$ (White)	205	14.13 (14.02)	16.30 (16.39)	56.00 (56.19)	9.64 (9.61)

significant change in the C-S and C=S stretching frequencies at 715 cm^{-1} and 1120-1055 cm^{-1}, respectively of the ligand indicating that the ligand is in the thiono form even after complexation[8]. However, the C-N absorption band[9] in the ligand at 1290 cm^{-1} is shifted in the complexes presumably due to an association of the ligand molecules in the solid phase which on complexation are dissociated causing it to appear at a lower frequency. A strong band at about 1380 cm^{-1}, absent in bismuthiol-I, is due to the νB-N[10].

In the far IR spectra of the complexes there is a new band of medium intensity at around 370-410 cm^{-1} which is absent in the free ligand. It is assigned to M-N stretching frequency suggesting coordination of the metal through the nitrogen atom of the bismuthiol-I.

Magnetic susceptibility and electronic spectra

In order to obtain information about the mode of coordination of the ligand around the metal ions and the ligand field strength, the magnetic moment of the complexes was measured and their reflectance spectra recorded.

The observed magnetic moment (3.61 B.M.) of the Cr(III) complex is slightly less than the expected value for an octahedral geometry. The bands at 23,809 and 16,129 cm^{-1} may reasonably be assigned to $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ and $^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$ transitions, respectively. These are the characteristic of an octahedral array of ligands around Cr(III) ion[11]. The ligand field parameters 10 *Dq*,*B* and β have been evaluated as 16,129 cm^{-1}, 721 cm^{-1} and 0.73 respectively.

The magnetic moment for square-planar Mn(II) ion in spin-free state is expected to be 5.92 B.M. while for spin-paired configuration, the magnetic moment ranges from 1.73 to 2.2 B.M. The magnetic moment value of 4.90 B.M. in the present case is lower than the spin-free and greater than the spin-paired moment. This intermediate value may, therefore, be regarded to be due to partial spin pairing as has also been observed in the manganous phthalocyanine complex. The reflectance spectrum of the Mn(II) complex in this case shows the strong charge transfer bands at 40,816 and 31,250 cm^{-1}. The band at 22,727 cm^{-1} is characteristic of a square-planar Mn(II) ion with the ground term $^4A_{1g}(b_{2g}^2, e_g^2, a_{1g}^1)$.

Reflectance spectrum of Fe(III) complex shows two absorption bands at 17,241 and 22,727 cm^{-1} assignable to $^4T_{1g}(G) \leftarrow {}^6A_{1g}$ and $^4T_{2g}(G) \leftarrow {}^6A_{1g}$ transitions, respectively, corresponding to an octahedral Fe(III) ion[12]. The magnetic moment value (5.83 B.M.) is slightly less than that calculated (5.92 B.M.) for an octahedral, high-spin Fe(III) ion. This deviation in $\mu_{eff.}$ value is probably due to antiferromagnetic effect. The 10 *Dq*, *B* and β values have been computed as 13,438 cm^{-1}, 905 cm^{-1} and 0.82 respectively.

A square-planar Co(II) complex commonly has a $\mu_{eff.}$ value between 2.1 and 2.8 B.M. The $\mu_{eff.}$ value of 2.75 B.M. and the charge-transfer band at 28,000 cm^{-1} (without the presence of any other band) also suggest a square-planar Co(II) complex[13].

The solid state reflectance spectrum of the Ni(II) complex exhibits one main band at 22,727 cm^{-1} assigned to $^1B_{1g} \leftarrow {}^1A_{1g}$ transition. The observed magnetic moment value of 2.27 B.M. also supports the square-planar geometry of Ni(II) ion[14].

A square-planar structure is proposed for the Cu(II) complex on the basis of the observed magnetic moment value (1.74 B.M.). The above geometry is supported by the presence of a weak band at 12,658 cm^{-1} attributable to $^2T_{2g} \leftarrow {}^2E_g$ transition[15].

The Zn(II) complex is diamagnetic as expected. From the stoichiometry, this complex is tentatively suggested to possess tetrahedral geometry, since tetrahedral geometry is a more preferred structure for Zn(II) complexes[16].

Acknowledgement

The authors (TAK and MAK) are grateful to the Head of the Department of Chemistry, Jamia Millia Islamia, New Delhi for encouragement. MAZ is thankful to CSIR, New Delhi for financial support.

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