Asian Journal of Chemistry Vol. 12, No. 3 (2000), 703–706

Magnetic Studies on Co(II) and Ni(II) Complexes of Hydroxamic Acid

N.N. JHA and INDRADEO PRASAD RAY*
Department of Chemistry
D.S. College, Katihar-854 105, India

The magnetic moment of a complex plays an important role in deciding the geometry of the complexes whether it is square-planar or tetrahedral or octahedral (outer or inner). The complex is diamagnetic; the possible structure is either square-planar or trigonal bipyramidal, but if the complex is paramagnetic, the possible structure is either tetrahedral or outer octahedral.

INTRODUCTION

Ni(II) ($3d^8$ configuration) generally forms square-planar, octahedral or tetrahedral complexes; strong ligand fields pair up the upaired electrons of Ni(II) complexes giving rise to formation of diamagnetic square-planar or trigonal bipyramidal complexes. Weak ligand gives rise to outer octahedral complexes, paramagnetic in nature, which are generally blue or green coloured .

The values of magnetic moment have been used successfully as a tool to distinguish between octahedral and tetrahedral configuration of the complexes of Ni(II) as well.

In octahedral field the triplet T_{2g} lies lower in energy than doublet e_g and the electronic configuration of the ground state may be written as $(T_{2g})^6(e_g)^2$. It is non-degenerate and not liable to John-Teller distortions and thus quite regular complexes are expected in case of six identical ligands.

The electrons of e_g levels are spin parallel and since there is no resultant orbital angular mement, once the degeneracy of the d-orbitals is lifted, magnetic moment should be close to the spin-only values of 2.8 B.M. However the first excited triplet level $^3T_{2g}$ has essentially the configuration $(T_{2g})^5(e_g)^3$. There are three possible ways of arranging the five T_{2g} electrons and the d_{yz} orbitals retain their rotational properties with respect to the z-axis. At this level, therefore, T_{2g} has orbital angular momentum and the spin-orbital coupling of Ni(II) is large enough to allow the mixing of this level with the lowest level to produce the true ground state. The effective result is that the orbital angular moment is not completely quenched by the ligand and the moments found for octahedral Ni(II) complexes are within the range of 2.83–3.4 B.M. and these values are independent of temperature.

In tetrahedral field the d-orbitals are split into a lower doublet (e_g) and an upper triplet (T_{2g}) giving the lowest configuration $(e_g)^4(T_{2g})^4$. The presence of four electrons in T_{2g} level leads to threefold degeneracy which brings forth two important consequences:

(1) That there are odd electrons partially distributed between the d_{yz} and d_{xz} orbitals which still retain their degeneracy and their rotational properties with respect to z-axis.

(2) That the orbital angular moment is accordingly not quenched by ligand field and thus magnetic moment normally found for tetrahedral Ni(II) complexes in the range 3.5–4.2 B.M. and are temperature independent.

Magnetic moments of a few Ni(II) complexes as reported by Blackhouse. Foss and Nylom are recorded here in Table-1.

TABLE-1
MAGNETIC MOMENT VALUES (B.M.)
OF Ni COMPLEXES (25°C)

Complex	μ_{eff}
$Ni(ET)_2Cl_2$	3.21
$Ni(ME)_2Br_2$	3.21
$Ni(ET)_2Br_2$	3.20
$Ni(ME)_2I_2$	3.22
$Ni(ET)_2I_2$	3.12

ET = 1,2-diethyl thioethane
ME = 1,2-dimethyl thioethane

Magnetic moment values of Ni(II) reported by Peach and Ramaswamy are in the range of 3.25–3.59 B.M. When they measured the magnetic moments of complexes of $NiCl_2(IT)_2$, $NiBr_2(IT)_2$ and $Ni(ClO_4)_2(IT)_2$ (where IT stands for isothiazole).

RESULTS AND DISCUSSION

In the present work, the magnetic moments recorded for different complexes of Ni(II) are given in Table-2.

TABLE-2

Sl. No.	Complexes	Colour	μ_{eff} (B.M.)
1.	$NiL_2{\cdot}2H_2O$	Pale green	2.94
2.	$NiL_2{\cdot}2H_2O$	Pale green	2.94
3.	NiL'Py(HCOO)	Faint green	Dimagnetic
4.	NiLPy(HCOO)	Faint green	Dimagnetic
5.	$NiL_2(\alpha\text{–Pic})_2$	Grey green	2.96
6.	$NiL'_2(\alpha\text{–Pic})_2$	Grey green	2.96
7.	NiL'_2Q_2	Green	2.96
8.	NiL_2Q_2	Green	2.99

L = 1-indenyl acetohydroxamic acid
L′ = *p*-methyl phenyl acetohydroxamic acid
Q = quinoline
Py = pyridine
α-Pic = α-picoline

The values of compounds 1, 2, 5, 6, 7 and 8 lie in the range of octahedral Ni(II) complexes, while values of compounds 4 and 5 lie in the range of square-planer complexes of Ni(II). The tetrahedral complexes may be excluded as they have high magnetic moments in the range of 3.5–4.2 B.M. at room temperature.

Magnetic behaviour of Co(II) Complexes

Cobalt(II) complexes with one unpaired electron may be either low spin octahedral or planar but complexes with three upaired electrons may be either octahedral or tetrahedral.[1]

High spin octahedral complexes of Co(II) have magnetic moments ranging from 4.7 to 5.2 B.M. They have large orbital contribution since the spin only formula for three unpaired electrons is only 3.88 B.M. This value is attributed to threefold orbital degeneracy $^4T_{1g}$ ground state. In a high spin tetrahedral complex the range is 4.3–4.7 B.M. which is temperature dependent.

The low spin tetrahedral Co(II) complexes exhibit moment values of 1.92–2.47 B.M. at room temperature which varies with temperature. The planar complexes have the same range. Complexes with values 2.5–4.3 B.M. have been also reported. Such complexes are viewed as anomalous.

Gosh and Banerjee[2] have found magnetic moments 4.15 to 4.60 B.M. in several bis-guanidine benzimidazole Co(II). They have proposed tetrahedral structures for them.

Bennister and Cotton[3] reported a blue coloured tetrahedral Co(II) complex $[\{(Me_2HC_6H_4)_3PO_4\}_4CO](ClO_4)$ to have magnetic moment 4.76 B.M.

Rande and Subba Rao[4] have measured magnetic moments of several carboxylates of Co(II). Values of Co(II) malonate, mandelate and tartarate lie between 5 to 5.22 B.M. Such complexes have been assigned high spin octahedral configurations. The Co(II) lactate has the value of magnetic moment 4.79 B.M which is supposed to have high spin tetrahedral geometry.

Gill and Nyholm[5] have reported several complexes of Co(II) and their magnetic moment values are given below in Table-3.

TABLE-3
OBSERVED MAGNETIC MOMENTS (B.M.) OF $CoX_2 \cdot 2Py$ at 20°C

Solid complex	Colour	μ_{eff}	Colour in Nitrobenezene	μ_{eff}
$CoCl_2 \cdot 2Py$	Violet	5.15	Blue	4.52
$CoBr_2 \cdot 2Py$	Blue	4.50	Blue	4.52
$CoI_2 \cdot 2Py$	Blue	4.47	Blue	4.59
$Co(CSN)_2 \cdot 2Py$	Purple red	5.10	Blue	4.50
$CoPy_2 \cdot Br_2 \cdot 2H_2O$	Violet	5.00	Blue	4.56

Stoufer *et al.*[6] have reported the magnetic moment values of several octahe-

dral Co(II) complexes but they fall in the range of 2.36 to 3.72 B.M as given in Table-4.

TABLE-4

	Compound	In B.M.	Temp. (K)
1.	$Co(terPyr)_2Br_2 \cdot H_2O$	2.63	295
2.	$Co(PBI)_2(BP_4)_2$	3.72	295
3.	$Co(BMI)_2(BF)_2$	2.291	295
4.	$Co(GdH)_2 \cdot Br_2$	3.16	295
5.	$Co(DTHP)(ClO_4)_2$	2.36	295

In the present work Co(II) complexes show magnetic moments between 3.24 to 4.26 B.M at room temperature as given in Table 5.

TABLE-5
OBSERVED MAGNETIC MOMENT VALUES OF Co(II) COMPLEXES

	Compound	Colour	μ_{eff} in B.M.
1.	$CoL'_2 \cdot 2H_2O$	Light pink	4.15
2.	$CoL_2 \cdot 2H_2O$	Bright pink	4.15
3.	$CoL'_2 \cdot Py_2$	Brown	4.06
4.	$CoL_2 \cdot Py_2$	Brown	4.07
5.	$CoL'_2 \cdot Q_2$	Brown	4.05
6.	$CoL_2 \cdot Q_2$	Brown	4.06
7.	$CoL_2(\alpha\text{-pic})_2$	Pink	3.24
8.	$CoL'_2(\alpha\text{-pic})_2$	Pink	3.24
9.	$CoL_2(\gamma\text{-pic})_2$	Pink	4.26
10.	$CoL'_2(\gamma\text{-pic})_2$	Pink	4.26

These values of magnetic moments of complexes of Co(II) suggest low spin octahedral or planar or high spin octahedral configurations for complexes.

The lower values of magnetic moments may be due to distortion present in the complexes and as magnetic susceptibility values could not be determined at various temperatures, so it is very difficult to arrive at any conclusion or to explain with certainty the cause for lower magnetic moment values of these complexes.

REFERENCES

1. B.N. Figgis and J. Lewis, Modern Coordination Chemistry.
2. S.P. Gosh and A.K. Banerjee, *Indian J.Chem.*, **2**, 294 (1964).
3. E. Beneister and F.A. Cotton, *J. Chem. Soc.*, 1876 (1960).
4. A.C. Rande and Subba Rao, *Indian J. Chem.*, **4**, 42 (1966).
5. N.S. Gill and R.S. Nyholm, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).
6. C. Stoufer, *Inorg. Chem.*, 1167 (1966).

(*Received*: 10 December 1999; *Accepted*: 25 January 2000) AJC-1984