Magnetic Study of Some Transition Metal Chelates with Thiolactic Anilide and Thiolactic *p*-Toluidide

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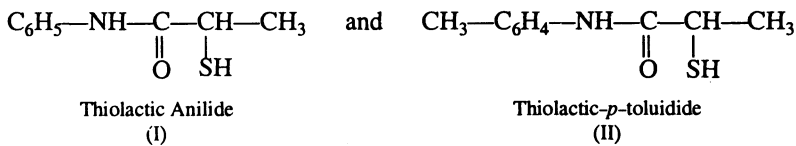*Department of Chemistry*
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A series of transition metal compounds with ligands, thiolactic anilide and thiolactic *p*-toluidide, containing heavier donor sulphur atom, have been synthesised. Characterisations of these compounds were made on the basis of their elemental analysis which showed that metal : ligands ratio is 1 : 2 in all the compounds. The electrical conductivities of these mono-nuclear compounds indicated herein suggest that the compounds are of complex nature. Magnetic studies of the complexes favour the octahedral symmetry of Co(II), Ni(II) and Cu(II) complexes. The other compounds of Hg(II), Pb(II) and Ag(I) are of diamagnetic behaviour.

INTRODUCTION

Metal complexes of ligands containing nitrogen, oxygen and sulphur have occupied a very active field of current researchers[1-5]. Though ligands containing nitrogen and oxygen have been studied since the beginning of the coordination chemistry but ligands with heavier donor atoms like phosphorus and sulphur have recently acquired considerable significance on account of their presence in biological systems and peculiar coordination behaviour. The data available on ligands having sulphur, oxygen and nitrogen, however, are not sufficient to afford a fairly coherent picture and thus offer scope for the present study.

In the present work, an attempt has been made to seek coordination between the metals with thiolactic anilide and thiolactic-*p*-toluidide and also their different physico-chemical properties.

$$C_6H_5-NH-\underset{\underset{O}{\|}}{C}-\underset{\underset{SH}{|}}{CH}-CH_3 \quad \text{and} \quad CH_3-C_6H_4-NH-\underset{\underset{O}{\|}}{C}-\underset{\underset{SH}{|}}{CH}-CH_3$$

Thiolactic Anilide   Thiolactic-*p*-toluidide
(I)   (II)

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EXPERIMENTAL

The organic reagents and solvents used in the present investigation were procured from B.D.H. and Bengal Chemicals.

Metal salts of nickel(II), cobalt(II), copper(II), mercury(II), lead(II) and silver(I) used were of either E. Merck (extra pure) or of B.D.H., A.R. quality.

Preparation of Ligands

Ligand I, thiolactic anilide[6], was prepared in a manner analogous to the preparation thioglycolanilide[7]. Equimolecular proportions of thiolactic acid and aniline (10.6 g thiolactic acid and 9.3 g aniline) were mixed in a 500 mL conical flask and heated in a glycerine bath maintained at about 120°C for about 2.5 h in a slow current of carbon dioxide gas. A solid product was obtained on pouring this mixture in enough water. It was filtered, crushed to powder in a mortar and washed initially with dilute hydrochloric acid and then with water to remove off excess aniline and thiolactic anilide respectively. The solid mass was crystallised in dilute alcohol and dried over conc. H_2SO_4 to give pure ligand, m.pt. 93°C.

The ligand II thiolactic-*p*-toluidide was prepared by the procedure analogous to the preparation of thiolactic anilide. Equimolecular proportions of thiolactic acid and *p*-toluidine (10.6 g thiolactic acid and *p*-toluidine) were mixed in a conical flask and heated on glycerine bath maintained at about 120°C for about 2 h in a slow current of carbons dioxide gas. The mixture on digestion was poured in enough water, filtered, crushed to powder and then washed with dilute hydrochloric acid and water to remove the unreacted starting materials. The mass was purified by repeated crystallisation in alcohol, m.pt. 132°C.

Preparation of metal complexes with ligand I

An aqueous solution of metal chlorides or sulphates (in case of lead and silver their acetates or nitrates were taken) were prepared in a minimum volume of water and made just alkaline (pH 5.0). The ethanolic solution of ligand was added slowly with continuous stirring to the desired metal salt solution. The precipitated chelate was digested on water bath for about 2.5 h and then filtered. The complex thus obtained was washed with ethanol and dried in vacuum desiccator.

Preparation of metal complexes with ligand II

Various metal complexes with *p*-toluidide were also prepared in the manner similar to described in thiolactic anilide case.

The stoichiometries of the metal complexes were established on the basis of their elemental analysis[8, 9] (Table-1).

Magnetic susceptibilities of the complexes were measured on a Gouy balance at room temperature. The effective magnetic moments (μ_{eff}) were calculated after making diamagnetic corrections using Pascal's constants and are tabulated (Table-2).

TABLE-1
ELEMENT ANALYSIS DATA OF COMPLEXES

S. No.	Complexes	Found (%)				
		M	C	H	N	S
1.	H-TLA	—	59.60	6.15	7.75	17.80
2.	Ni(TLA)$_2$·2H$_2$O	12.92	47.43	5.30	6.19	14.00
3.	Co(TLA)$_2$·2H$_2$O	12.90	47.48	5.35	6.10	14.01
4.	Cu(TLA)$_2$·2H$_2$O	13.84	46.98	5.28	6.10	13.90
5.	Hg(TLA)$_2$	35.72	35.84	3.60	4.92	11.48
6.	Ag(TLA)	37.42	37.42	3.54	4.84	11.15
7.	H-TLPT Ligand II	—	61.46	6.74	7.16	16.45
8.	Ni(TLPT)$_2$·2H$_2$O	12.18	49.65	5.86	5.75	13.30
9.	CO(II) Complex Co(TLPT)$_2$·2H$_2$O	12.17	49.66	5.85	5.77	13.28
10.	Cu(TLPT)$_2$·2H$_2$O	13.00	49.20	5.78	5.70	13.10
11.	Hg(TLPT)$_2$	34.04	40.72	4.10	4.75	10.88
12.	Pb(TLPT)$_2$	34.80	40.35	4.02	4.72	10.79

TLA—Thiolactic anilide; TLPT—Thiolactic-*p*-toluidide

TABLE-2
FORMULAE, MAGNETIC MOMENTS, ELECTRICAL
CONDUCTIVITIES AND MOLECULAR WEIGHTS OF METAL COMPLEXES

Formulae of complexes	Magnetic moment values μ_{eff} (B.M.)	Electrical conductivity m (ohm^{-1} mol^{-1} cm^{-1})	m.w.
Ni(TLA)$_2$·(H$_2$O)$_2$	3.10	12	455.04
Co(TLA)$_2$·(H$_2$O)$_2$	4.98	20	455.26
Cu(TLA)$_2$·(H$_2$O)$_2$	1.84	15	459.87
Hg(TLA)$_2$	Diamagnetic	06	560.89
Ag(TLA)	Diamagnetic	08	288.02
Ni(TLPT)$_2$·(H$_2$O)$_2$	3.00	10	483.07
Co(TLPT)$_2$·(H$_2$O)$_2$	5.10	15	483.29
Cu(TLPT)$_2$.(H$_2$O)$_2$	1.88	12	487.90
Hg(TLPT)$_2$	Diamagnetic	06	588.92
Pb(TLPT)$_2$	Diamagnetic	14	595.52

RESULTS AND DISCUSSION

Magnetic moment values of Co(II) complexes lie between 1.80 and 5.2 B.M.[10] The complexes of cobalt(II) of coordination number four, five and six are well established; however, coordination number four and six are more common. The complexes of cobalt(II) of coordination number four are observed in both the planar (dsp^2) and tetrahedral symmetry. In the present investigation the magnetic moment values for bisligated complexes of cobalt(II) Co(TLA)$_2$·2H$_2$O and Co(TLPT)$_2$·2H$_2$O were observed to be 4.98 B.M. and 5.10 B.M. respectively and fall in the range of octahedral cobalt(II) complexes. On the basis of these moment values it is concluded that the complexes are of high spin octahedral symmetries. It is claimed recently that planar complexes of type CoO$_4$ may be of higher spin and have effective values in the range 4.8–5.2 B.M.[11, 12] but possibilities have been indicated that compounds are in reality octahedral due to intermolecular association[13].

The effective magnetic moment 3.1 B.M. for Ni(TLA)$_2$.2H$_2$O is within the limits of magnetic moments theoretically predicted for octahedral geometry and as such may have octahedral symmetry. The effective magnetic moment value 3.1 B.M. is also within the limits specified for square planar configuration. In octahedral envoronment, the same may also be considered to be square planar through the ionic group of ligands lying above and below the plane[14, 15]. The paramagnetic square complexes, however, are too rare and as such this possibility is not feasible. Moreover, the magnetic moment values in case of tetrahedral geometry should always be higher than 3.2 B.M., the lowest limit reported in text books. Thus the compound being of tetrahedral geometry is not plausible. Higher value of moment 3.1 B.M. may be attributed to Jahn-Teller distortion of octahedral structure acquiring D$_{4h}$ symmetry. On the basis of similar arguments the nickel(II) complex with thiolactic-p-toluidide having moment value 3.0 B.M. may also be assigned to have distorted octahedral geometry.

Magnetic moment values of copper(II) complexes reported earlier have been broadly categorised into two groups:

(i) those having magnetic moment values in the range 1.75–2.20 B.M. at room temperature.

(ii) these having magnetic moment values substantially between 0.0 to 1.73 B.M. and are temperature dependent. In such complexes the pair of copper atoms are held together closely through bridging halogens, hydroxy, carboxylate and ligand molecules[16–18]. Some of the copper(II) complexes in which copper(II) ions are coupled to form dimers are observed either diamagnetic or possess subnormal magnetic moments[19, 20]. In case of mononuclear complexes there is no major interaction of unpaired electrons of different copper ions and as such moment values are independent of temperature. Theoretically there should be some correlation between the magnitude of orbital contribution and geometry of compounds, but in practice the relation is seldom recorded.

Ray and Sen[21] studied the magnetic moment values of a fairly large number of copper(II) compounds of the afore mentioned category and divided them into two subclasses, $i.e.$, moment values 1.72–1.82 B.M. for square planar and to 0.88–2.20

B.M. for tetrahedral or octahedral compounds of copper(II). The present values of both copper(II) complexes, *i.e.*, $Cu(TLA)_2 \cdot 2H_2O$ and $Cu(TLPT)_2 \cdot 2H_2O$, *i.e.*, 1.84 and 1.88 B.M. respectively thus indicate that the complexes are magnetically dilute at room temperature and possess distorted octahedral structure.

Magnetic behaviour of Hg(II), Pb(II), Pb(II) and Ag(I) complexes as expected are diamagnetic.

ACKNOWLEDGEMENTS

REFERENCES

1.   S. Ahrland, J. Chat and N.R. Davies, *Quart. Rev.*, **12**, 265 (1958).

2.   S.E. Livingstone, *Quart. Rev.*, London, **19**, 408 (1965).

3.   _____, *Coord. Chem. Rev.*, **7**, 59 (1971).

4.   M. Akbar Ali and S.E. Livingstone, *Coord. Chem. Rev.*, **13**, 101 (1974).

5.   D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 233 (1971).

6.   R.N. Mishra, Sircar, and S.S. Guha, *J. Indian Chem. Soc.*, **33**, 523 (1956).

7.   _____, *J. Indian Chem. Soc.*, **32**, 127 (1955).

8.   A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longmans Green & Co., Ltd., London (1952).

9.   F.J. Welcher, Organic Analytical Reagents, Vol. I & II, D.Von Nostrand Co. Inc., New Jersey (1948).

10.   D.H. Busch, in: R.S. Young (Ed.), Cobalt, Chapter 6, A.C.S. Monograph Series, Reinhold Publishing Corp., New York (1960).

11.   B.N. Figgis and J. Jewis, *Prog. Inorg. Chem.*, **6**, 37 (1964).

12.   L.M. Venanzi, *J. Chem. Soc.*, 719 (1958).

13.   N.S. Gill and R.S. Nyholm, *J. Chem. Soc.*, 3397–98 (1959).

14.   G. Maki *J. Chem. Phys.*, **28**, 651 (1958).

15.   _____, *J. Chem. Phys.*, **29**, 151 (1959).

16.   M. Kishita, M. Inoue and M. Kubo *Inorg. Chem.*, **3**, 237 (1964).

17.   S.E. Livingstone *Quart. Rev.*, London, **19**, 386 (1965).

18.   L.N. Martin and H. Waterman, *J. Chem. Soc.*, 2545 (1957).

19.   T. Norita, *Soumen Kem*, **33**, 161 (1960).

20.   M. Kets, H.B. Jonassen and T.C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

21.   P. Ray and D. Sen, *J. Indian Chem. Soc.*, **25**, 473 (1948).