Spectral & Magnetic Studies of Complexes of Bis-(dimethylglyoximato)cobalt(II) with Thioureas

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Diaquo-bis(dimethylglyoximato)cobalt(II) reacts with sulphur donating ligands to form hexacoordinated mixed ligand complexes having the general formula Co(dimethylglyoximate)$_2$L$_2$ where L is a sulphur donating ligand. Analytical, magnetic, infrared and electronic spectral data indicate that the complexes are slightly distorted due to non-identical nature of the coordinating atoms and have one unpaired electron required for low spin complexes. The values of parameter *B* and 10 *Dq* have been calculated using equations following strong field coupling scheme.

COBALOXIMES or bis-dimethylglyoximatocobalt (II) resemble very closely vitamin B_{12} derivatives. Several papers have been published on their synthesis and chemical characteristics[1]. Generally cobalt(II) complexes show tendency toward atmospheric oxidation, but bis-dimethylglyoximato cobalt(II) has been found to be quite stable. Hence it was considered worthwhile to study the synthesis and characteristics of mixed ligand derivatives of bis-dimethylglyoximatocobalt(II) with thiourea and substituted thioureas.

All the chemicals used were of AR grade. Diaquo-bis-(dimethylglyoximato)cobalt(II) was prepared[2] and its purity checked by elemental analyses.

Preparation of mixed ligand complexes — a solution of stoichiometric amount (0·02 mol) of the ligand in minimum volume of ethanol was added to a solution of diaquo-bis-dimethylglyoximato cobalt(II) (0·01 mol) dissolved in minimum volume of ethanol under nitrogen atmosphere. The resulting solution was refluxed slowly for 1 hr under N_2 atmosphere. The microcrystalline solid separated was filtered, washed with ethanol and dried *in vacuo*. The purity of the complexes was established by elemental analysis by standard methods.

Complexes are light brown to dark brown in colour. The thiourea, phenylthiourea and diphenylthiourea derivatives do not melt up to 350° while the methylthiourea and benzoylthiourea derivatives melt with decomposition at 238° and 244° respectively. Analysis and magnetic moments (Gouy method at 300° ± 1° K) are summarized in Table 1 and the electronic spectral data in Table 2.

In weak field the experimentally observed spin allowed transitions in cobalt(II) are in order of increasing energy via ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$; while in strong field the experimentally observed spin allowed transitions are in order of increasing energy viz. ${}^2E_g \rightarrow {}^4T_{1g}$, ${}^2E_g \rightarrow {}^2T_{1g}$ and ${}^2E_g \rightarrow {}^2T_{2g}$. These transitions are denoted by ν_1, ν_2 and ν_3 respectively in both weak and strong field. In the present study of spin paired cobalt(II) complexes, the transition ${}^2E_g \rightarrow {}^2T_{2g}$ occurs as a shoulder in the region 20,000-22,000 cm^{-1}, designated as ν_3. This assignment is based on a similar band at 20,000 cm^{-1} in hexaaquo cobalt(II) ion[3]. A small broad absorption band in some cases and a distinct band in others, corresponding to the transition ${}^2E_g \rightarrow {}^2T_{1g}$ (ν_2) as found $\sim$ 17,850 cm^{-1} in hexaaquocobalt(II) ion, occurs in the region 15,700-16,500 cm^{-1}. The pattern of absorption spectra of these complexes has been found to be similar to hexaaquocobalt(II) ion suggesting thereby that the stereochemistry of metal ion of both type of species are almost identical. Slight distortion from idealized octahedral stereochemistry can be visualized in the view of the non-identical nature of the coordinating atoms. This finds support from the existence of two bands in the region 15,000-20,000 cm^{-1} to which is generally attributed the

TABLE 1 — ANALYSES AND MAGNETIC MOMENT DATA

Complex	Found (Calc.) (%)			μ_{eff} B.M.
	Metal	N	S	
$Co(DH)_2(H_2O)_2$	(18·12) 18·1	(17·23) 17·1	—	1·74
$Co(DH)_2(Tu)_2$	(13·35) 13·3	(25·38) 25·1	(14·52) 14·4	1·79
$Co(DH)_2(MeTu)_2$	(12·55) 12·4	(23·87) 23·6	(13·66) 13·6	1·81
$Co(DH)_2(PhTu)_2$	(9·92) 9·8	(18·87) 18·7	(10·78) 10·6	1·92
$Co(DH)_2(BenzTu)_2$	(9·07) 8·8	(17·26) 17·1	(9·87) 9·7	1·95
$Co(DH)_2(DiphTu)_2$	(7·90) 7·8	(15·03) 14·9	(8·60) 8·7	Diamagnetic

DH = dimethylglyoxime, Tu = thiourea, MeTu = methylthiourea, PhTu = phenylthiourea, BenzTu = benzoylthiourea, DiphTu = diphenylthiourea.

TABLE 2 — EXPERIMENTAL TRANSITION ENERGIES, CALCULATED VALUES FOR PARAMETER *B*, 10*Dq* β AND ν_3/ν_1 OF THE SPIN ALLOWED BAND IN OCTAHEDRAL SPIN PAIRED Co(II) COMPLEXES

Complex	ν_1	ν_2	ν_3	*B* cm^{-1}	β	ν_3/ν_1	10 *Dq* cm^{-1}
$Co(DH)_2\ (H_2O)_2$	10050	16447	21978	551·66	0·567	2·1868	11928
$Co(DH)_2\ (Tu)_2$	10204	15974	20964	421·73	0·433	2·0544	10760
$Co(DH)_2\ (MeTu)_2$	10309	15822	20618	367·53	0·378	2·0000	10309
$Co(DH)_2\ (PhTu)_2$	10416	15923	20920	373·00	0·383	2·0084	10504
$Co(DH)_2\ (BenzTu)_2$	10101	15873	20964	435·60	0·448	2·0754	10563
$Co(DH)_2\ (DiphTu)_2$	10638	16260	20408	316·93	0·359	1·9184	9770

splitting[4] of the band as a result of distortion. The spectra of bis-cobaloxime have been reported by Nadezhina and Kovalenko[5], the position of lowest transition, $^2E_g \rightarrow {}^4T_{1g}$, ($\nu_1$) being in the region 10,000-10,650 cm^{-1}. The value of Racah's parameter B calculated[6] following strong field coupling is in the range 317-550 cm^{-1} as compared to 972 cm^{-1} for cobaltaquo ion[7]. Naturally its contribution towards nephelauxetic ratio, β (0·35 to 0·56) is low indicating increase in covalency. The values of 10 *Dq* (difference of ν_3 and ν_1 transition in strong field) for these mixed ligand complexes are in the range of 9770 to 11928 cm^{-1} and that of ν_3/ν_1 ratio in the range 1·9184-2·1868. Electronic spectral data and calculated values for parameter B and 10 *Dq* (in cm^{-1}), β and ν_3/ν_1 ratio are given in Table 2.

The value of magnetic moment (μ_{eff}) of the complexes are in the range of 1·74 to 1·95 B.M., suggesting the presence of one unpaired electron[8] and hence complexes are spin paired complexes. However, the diphenylthiourea derivative has been found to be diamagnetic. The diamagnetic nature of this complex may be due to metal-metal bonding[9,10].

Infrared spectrum of diaquo-bis-dimethylglyoximatocobalt(II) exhibits coordinated water molecules at 3440 cm^{-1}. This band is absent in the presently prepared complexes, indicating these to be anhydrous. The changes in ν (M-N) occur around 510 cm^{-1}, while absorption due to ν (C-N) ($\sim$1070 cm^{-1}) and ν (N-O)[11] (1540-1580 cm^{-1}) undergo slight shift from similar absorption in parent complex. The bands of dimethylglyoxime and thioureas are modified, indicating that both the ligands are bonded to metal. According to Bailey and Pearson[12] and others, large increase in ν (N-H) and amide-II vibrations and small shift in δ (NH$_2$) vibration indicate S-bonding to metal ion. In the present complexes the shift in ν (N-H) by 10-60 cm^{-1}, in amide-II vibrations by 15 cm^{-1} and in δ (NH$_2$) vibration by 3-5 cm^{-1} support the coordination of metal through sulphur atom of thiourea ligand.

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Synthesis & Characterization of Some Dibutylmetal(III) Pseudohalides

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Some hitherto unknown pseudohalides of the formula Bu$_2$MX (M=Ga, In or Tl; X=N$_3$, NCO, NCS or NCSe) have been synthesized in quantitative yield through metathetical reaction between Bu$_2$MCl and the corresponding alkali metal salts. The compounds have been characterized by their elemental analyses and IR data. The azides are thermally stable and do not explode at their melting points. Infrared data are presented in support of their structures.

As compared to extensively studied pseudohalides of non-transition metals of Group IV[1-3] (R$_3$MX, R = an organic group; X = N$_3$, NCO or NCS, M = Ge or Sn), similar compounds of Group III metals (R$_2$MX, M = Ga, In or Tl) have received little attention. Mueller *et al.*[4] reported the preparation of some dialkyl azides of aluminium, gallium, indium and thallium by the interaction of chlorine azide with corresponding metal trialkyls. Srivastava and coworkers reported the preparation and characterization of some diaryl thallium cyanides[5], azides[6] and selenocyanates[7]. Infrared studies of R$_2$TlNCS (R = Me, Et or Ph) and PhTl (N$_3$)$_2$[8] have also been reported. We now report the synthesis and characterization of some dibutylmetal(III) pseudohalides, Bu$_2$MX (M = Ga, In or Tl; X = N$_3$, NCO, NCS, NCSe).

Dibutylgallium, indium and thallium chlorides were prepared by the interaction of metal(III) chlorides and dibutyltin dichloride.

In a typical experiment, to a boiling solution containing a mixture of dibutyltin dichloride (1 mmol) and tetrahydrated metal(III) chloride in 40 ml methanol/ethanol, was added aqueous sodium hydroxide (30 ml, 20%) and the mixture refluxed. The resulting mixture was cooled and hydrochloric acid (60 ml, 15%) added with constant stirring. The solid product was filtered, washed with ethanol and finally with diethyl ether and dried at 90°. The product was recrystallized from the same solvent.

Dibutylmetal(III) pseudohalides were obtained by stirring dibutylmetal chloride with the corresponding alkali metal salt, at room temperature, in pyridine-water (1 : 1) mixture for 1 to 3 hr. The solid was filtered, washed with ethanol-water and dried *in vacuo*.

All the pseudohalides have been prepared through metathetical reaction $Bu_2MCl + M'X \rightarrow Bu_2MX +$