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Infrared studies on molecular association of metal thiocarboxamide complexes with iodine and silver perchlorate

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ABSTRACT

The charge transfer complexes were prepared and characterized by I.R. and elemental analysis. The molecular formula were found to be Co $(ETH)_2$- I_2, Ni $(ETH)_2$- I_2, Cu $(ETH)_2$- I_2, Zn $(ETH)_2$- I_2, Co $(ETH)_2$- $AgClO_4$, Ni $(ETH)_2$- $AgClO_4$, and Zn $(ETH)_2$ - $AgClO_4$,.

Key words: Metal thiocarboxamide complexes, Iodine, Silver perchlorate.

INTRODUCTION

In our previous communication[1], we reported the dielectric properties of metal thiocarboxamide complexes and their molecular complexes with iodine. In order to suggest a probale structure of metal thiocarboxmide-I_2 complexes we carried out I.R. spectral studies and interpret the structure with the help of I.R. frequencies undergoing major changes after the formation of adduct.

EXPERIMENTAL

Materials

Metal thiocarboxamide complexes have been prepared by the procedure elsewhere[2].

All melting points were taken on Fisher Johns melting point apparatus and are uncorrected. The recrystallized product were kept in vacuum desiccators for 2-3 weeks in order to remove last traces of solvent. Identities of the products were established on the basis of I.R. spectral data, mixed melting points and elemental analyses. The analyses of the metal ions in the complexes were carried out by standard methods.

Spectral measurements

Infrared spectral were recorded on a Perkin-Elmer Model 521 in the 4000-50 cm^{-1} regions. Samples were prepared in KBr disc. Calibration of frequency reading was made with polystyrene film.

Preparation of adducts

Co $(ETH)_2$-I_2 1.02g (0.005 M), of complex was dissolved in carbon tetrachloride complex was dissolved in carbon tetrachloride (20 ml) and a solution of iodine, 0.245g (0.01 M) in carbon tetrachloride (20 ml) was added to it slowly with constant stirring. Yellowish brown coloured precipitate that separated after keeping the reaction mixture for 10 minutes at room temperature, was filtered under suction and washed with carbon tetrachloride. Yield 95% of the theoretical. An analytical yellow coloured sample, mp 150°C, was obtained by recrystallization form 60% ether.

Ni $(ETH)_2$ – I_2 0.75g (0.01M), of complex was dissolved in carbon tetrachloride complex was dissolved in carbon tetrachloride (25 ml) and a solution of iodine, 0.254g (0.01 M) in carbon tetrachloride (25 ml) was added to it slowly with constant stirring. Light brown precipitate that separated after keeping the reaction mixture of

20-30 minutes was filtered under suction and washed with carbon tetrachloride. Yield 85% of the theoretical. An analytical sample, mp 200°C, was obtained by recrystallization form petroleum ether.

Cu (ETH)$_2$ – I$_2$ 0.62g (0.01M), of complex was dissolved in carbon tetrachloride complex was dissolved in carbon tetrachloride (10 ml) and a solution of iodine, 0.254g (0.01 M) in carbon tetrachloride (10 ml) was added to it with constant shaking at room temperature. The product rapidly and almost quantitatively precipitated from reaction mixture. The compound readily sublime and it has been characterized by elemental analyses and I.R. Spectra.

Zn (ETH)$_2$ – I$_2$ 0.68g (0.01M), of complex was dissolved in carbon tetrachloride complex was dissolved in carbon tetrachloride (15 ml) and a solution of iodine, 0.254g (0.01 M) in carbon tetrachloride (15 ml) was added to it slowly with constant stirring. Dark brown precipitate that separated after keeping the reaction mixture of 15-20 minutes was filtered under suction and washed with carbon tetrachloride. Yield 90% of the theoretical. An analytical sample, mp 210°C, was obtained by recrystallization form petroleum ether.

Co (ETH)$_2$ – AgClO$_4$ the 1.00g (0.005M) was dissolved in benzene (10 ml) and the solution of silver perchlorate, 0.5g in benzene (10ml) was added with constant stirring. Brown crystal that separated after keeping the reaction mixture for 15 minutes were filtered under suction and washed with benzene. Yield 98% of the theoretical. An analytical sample, mp 210°C, was obtained by recrystallization form petroleum ether.

	Carbon	Hydrogen	Nitrogen	Sulphur	Iodine	Metal (Co)
%Found	18.7088	1.9768	5.5802	6.2628	49.7128	11.5344
%Calculate	18.7891	1.9572	5.4801	6.2630	49.7129	11.5343

	Carbon	Hydrogen	Nitrogen	Sulphur	Iodine	Metal (Ni)
%Found	18.7078	1.9878	5.5824	6.3462	49.8368	11.5938
%Calculate	18.7977	1.9581	5.4826	6.2659	49.7357	11.4938

	Carbon	Hydrogen	Nitrogen	Sulphur	Iodine	Metal (Cu)
%Found	18.5814	1.9698	5.5314	6.2974	49.2784	12.3462
%Calculate	18.6210	1.9396	5.4311	6.2070	49.2681	12.3259

	Carbon	Hydrogen	Nitrogen	Sulphur	Iodine	Metal (Zn)
%Found	18.4838	1.9618	5.4588	6.2114	49.1632	12.7108
%Calculate	18.5435	1.9316	5.4085	6.1811	49.0631	12.6907

Ni (ETH)$_2$ – AgClO$_4$ the 1.02g (0.003M) was dissolved in toluene (15 ml) and the solution of silver perchlorate, 0.5g in benzene (10ml) was added with constant stirring. Green coloured crystal that separated after 10 minutes were filtered under suction and washed with benzene. Yield 90% of the theoretical. An analytical sample, mp 215°C, was obtained by recrystallization form petroleum ether.

Cu (ETH)$_2$ – AgClO$_4$ 0.55g (0.01M) of complex dissolved in toluene (15 ml) and the solution of silver perchlorate, 0.5g in benzene (15ml) was added with

constant stirring at room temperature. The product rapidly and almost quantitatively precipitated from the reaction mixture after one half an hour. This were filtered under suction and washed with benzene. Yield 92% of the theoretical. An analytical sample, mp 220°C, was obtained by recrystallization form petroleum 60% ether.

Zn (ETH) $_2$ – AgClO$_4$ 0.54g (0.01M) of complex was dissolved in toluene (15 ml) and the solution of silver perchlorate, 0.5g in benzene (15ml) was added with constant stirring. Light Green crystal that separated after 15 minutes, were filtered under suction and washed with benzene. Yield 95% of the theoretical. An analytical sample, mp 215°C, was obtained by recrystallization from alcohol.

	Carbon	Hydrogen	Nitrogen	Chlorine	Sulphur	Silver	Metal (Co)
%Found	20.5762	2.1638	6.1010	7.6660	6.9122	23.2130	12.7130
%Calculate	20.6761	2.1537	6.0305	7.6458	6.8920	23.2326	12.6927

	Carbon	Hydrogen	Nitrogen	Chlorine	Sulphur	Silver	Metal (Ni)
%Found	20.5868	2.1848	6.1136	7.6598	6.9458	23.2146	12.6688
%Calculate	20.6865	2.1548	6.0335	7.6497	6.8955	23.2443	12.6487

	Carbon	Hydrogen	Nitrogen	Chlorine	Sulphur	Silver	Metal (Cu)
%Found	20.3830	2.1628	5.9516	7.5908	6.8844	22.9846	13.0518
%Calculate	20.4727	2.1325	5.9712	7.5706	6.8242	23.0041	13.5516

	Carbon	Hydrogen	Nitrogen	Chlorine	Sulphur	Silver	Metal (Zn)
%Found	20.2794	2.1830	5.8440	7.6362	6.8132	22.5412	13.6468
%Calculate	20.3791	2.1228	5.9439	7.5360	6.7930	22.8989	13.9469

RESULTS AND DISCUSSION

Metal thiocarboxamide and I_2 system

The principal I.R. absorption frequencies of molecular complexes of these metal chelates with iodine are recorded in Table-1. The spectra of the molecular complexes are closely similar to each other[3-8]. The spectra of the molecular compounds contain bands of similar intensity with energies, which vary by only about ± 10cm^{-1}. Furthermore, these compounds exhibit band intensities and energies less than those exhibited by the parental compounds. On complexation a reduction of 20-25 cm^{-1} in these stretching frequencies was observed as compared to free ligand. No appreciable effect on other stretching frequencies of metal thiocaboxamide complexes was observed on complexation with iodine. The observed appreciable effect on the C⋯O and C⋯N stretching frequencies may be interpreted in terms of π- type complexing between metal chelate and the iodine.

The infrared spectra of the solid Co (ETH) $_2$-I_2 have been studied in detail in the region 4000-250cm^{-1} using KBr disc. The I.R. spectra of all metal thiocarboxamide-iodine complexes exhibits four bands, three in the region 1500-1000 cm^{-1}, exhibited by the iodine compound. These data strongly

indicated that these complexes have similar structures and the that each contains at approximately planar M $(ETH)_2$ moiety.

On the basis of above I.R. spectral studies following type of structure is proposed for metal thiocarboxamide-I^2 addcut.

Metal thiacarboxamide-$AgClO_4$ complexes

The infrared spectra of metal thiocarboxamide I_2 and their molecular complexes with silver perchlorate are recorded in table-2. The spectra of the M $(ETH)_2$ $AgClO_4$ are closely similar to each other and also to that M $(ETH)_2$. The spectra of the M $(ETH)_2$ $AgClO_4$ compounds contain bands of similar intensity with energies which vary slightly. The most effected stretching frequencies on complexation with silver perchlorate are C⋯O and C⋯N stretching frequencies near 1530-1550 cm^{-1}.

On complexation a reduaction of 15-20 cm^{-1} in these stretching frequencies was observed. No appreciable effect on the stretching frequencies of $M(ETH)_2$ complexes was observed on complexation with iodine. The observed appreciable effect on the C⋯O and C⋯N stretching frequencies may be interpreted in terms of a sacrificial role of the metal thiocaboxamide in the complexes. Further, the effects on the stretching frequencies also depend on the metal present in the chelate ring. Thus from the I.R. spectra we can interpret that the order of effect on the stretching frequencies C⋯O and C⋯N on complexation follows the order.

Co $(ETH)_2$> Ni $(ETH)_2$> Cu $(ETH)_2$> Zn $(ETH)_2$

The other four bands observed near 462,628,935 and 1102 in the spectra of these solid adducts are due to silver perchlorate.

Thus from these results we can draw a conclusion the metal thiocarboxamide chelate rings behave in similar manner a benzene ring does.

Table -1: Infrared absopriton stretchng frequencies (cm^{-1}) of metal thiocarboxamide complexes wiht iodine

Co $(ETH)_2$-I_2	Ni $(ETH)_2$-I_2	Cu $(ETH)_2$-I_2	Zn $(ETH)_2$-I_2	Possible assignment
3349	3343	3340	3339	N-H Stretching
1742	1739	1735	1733	C⋯O Stretching
1560	1554	1550	1525	Thioamide band I + amide band II
1535	1531	1528	1525	C⋯C Str. Coupled with C-H in plane bending mode
1389	1385	1380	1377	CH_3 deg. def.
1377	1373	1370	1367	C⋯O str. coupled with C-H bending mode.
1339	133	1330	1327	Thioamide band II + amide band III
1292	1289	1285	1280	CH_3 sym. deformation.
1229	1224	1220	1218	C⋯O Str.
1208	1203	1200	1195	C⋯C str. coupled with C-CH_3 str. mode
1029	1025	1020	1018	C-H in plane blending
1020	1017	1012	1009	CH_3 rocking
864	860	855	850	C = S str.
783	779	775	772	C- H out of plane bending
692	689	685	683	M-O str. + ring deformation
632	628	625	622	N-H bending out of plant
489	484	480	477	M⋯O str.
430	354	350	347	M⋯S str.
168	165	163	161	I-I str.

Table -2: Infrared absopriton stretchng frequencies (cm^{-1}) of metal thiocarboxamide complexes wiht silver perchlorate

Co $(ETH)_2$-$AgClO_4$	Ni $(ETH)_2$-$AgClO_4$	Cu $(ETH)_2$-$AgClO_4$	Zn $(ETH)_2$-$AgClO_4$	Possible assignment
3339	3337	3335	3333	N-H Stretching
1734	1733	1731	1729	C⋯O Stretching
1553	1551	1547	1542	Thioamide band I + amide band II
1530	1531	1528	1525	C⋯C Str. Coupled with C-H in plane bending mode
1385	1382	1380	1378	CH_3 deg. def.
1373	1371	1369	1367	C⋯O str. coupled with C-H bending mode.
1335	1333	1321	1319	Thioamide band II + amide band III
1289	1287	1284	1280	CH_3 sym. deformation.
1225	1223	1221	1219	C⋯O Str.
1202	1200	1198	1197	C⋯C str. coupled with C-CH_3 str. mode
1025	1023	1020	1018	C-H in plane blending
1018	1015	1013	1011	CH_3 rocking
862	860	859	857	C= S str.
780	778	775	773	C- H out of plane bending
690	687	684	682	M-O str. + ring deformation
629	627	626	623	N-H bending out of plant
485	483	481	479	M⋯O str.
358	356	353	351	M⋯S str.
350	345	340	338	AgCl str.

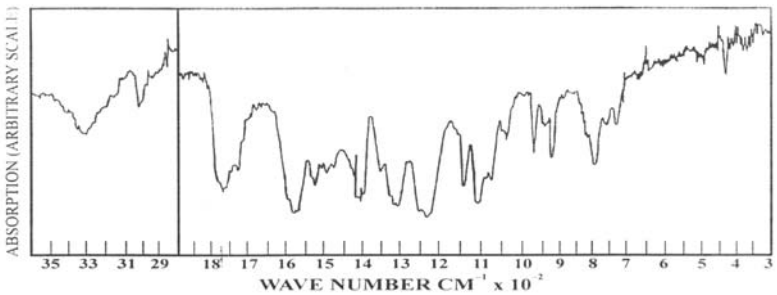

Fig. -1.1: Infrared spectra of $Co(ETH)_2$-I_2 in KBr disc

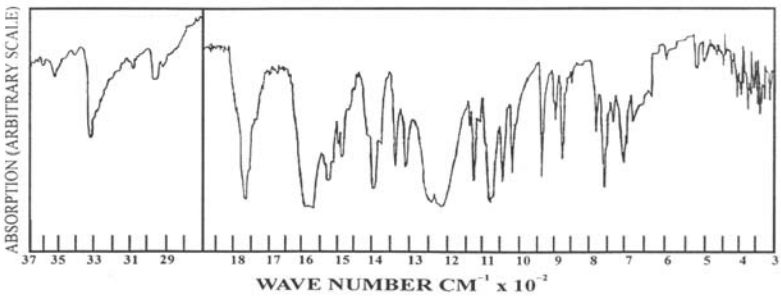

Fig. -1.2: Infrared spectra of $Ni(ETH)_2$-I_2 in KBr disc

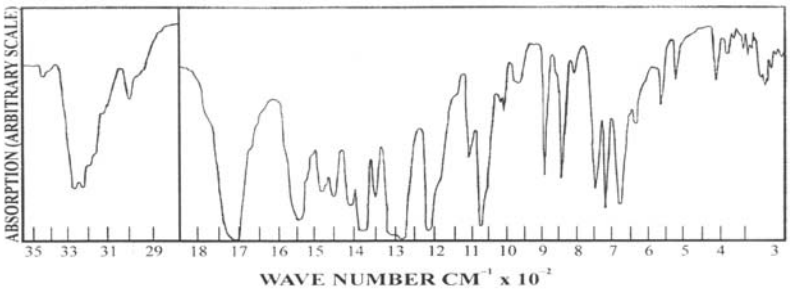

Fig. -1.3: Infrared spectra of $Cu(ETH)_2$-I_2 in KBr disc

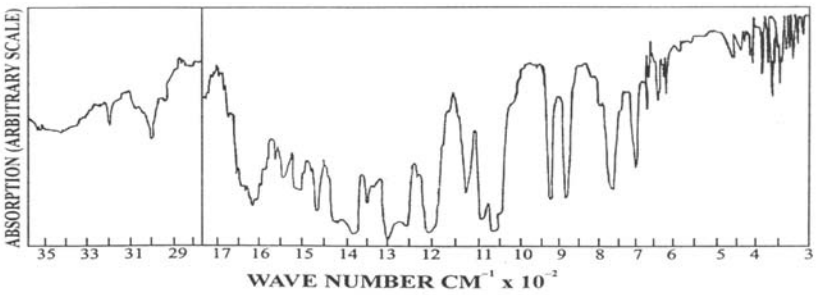

Fig. -1.4: Infrared spectra of $Zn(ETH)_2$-I_2 in KBr disc

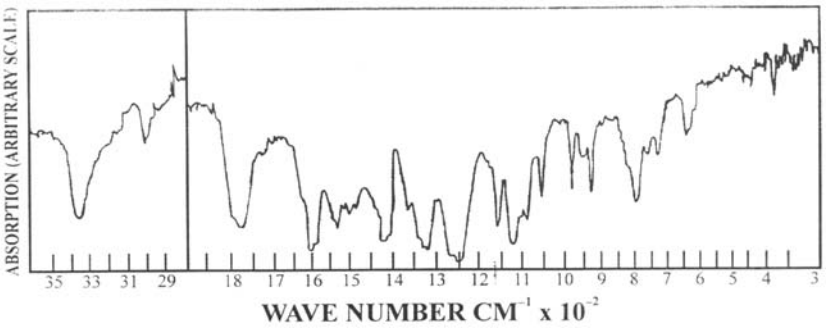

Fig. -2.1: Infrared spectra of $Co(ETH)_2$-$AgClO_4$ in KBr disc

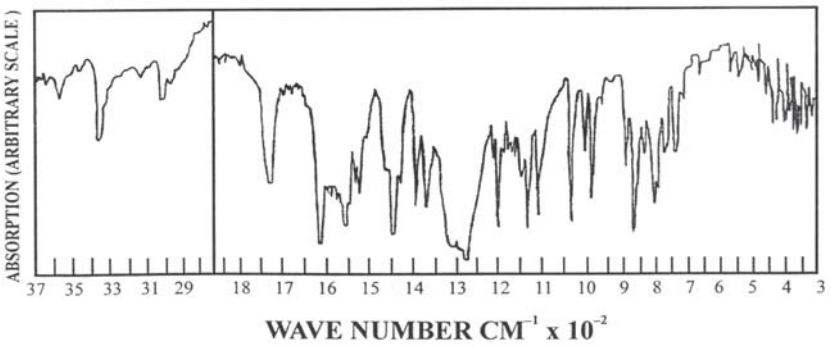

Fig. -2.2: Infrared spectra of $Ni(ETH)_2$-$AgClO_4$ in KBr disc

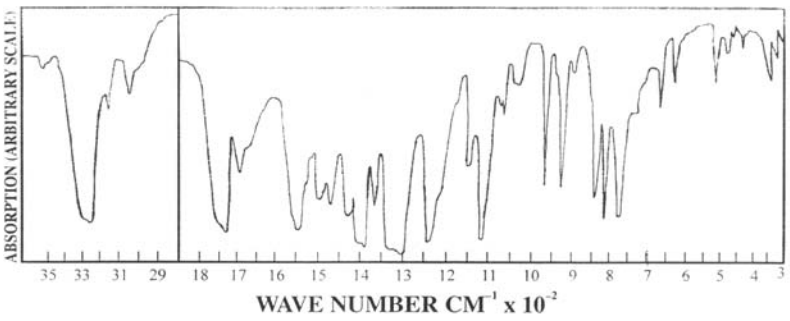

Fig. -2.3: Infrared spectra of $Cu(ETH)_2$-$AgClO_4$ in KBr disc

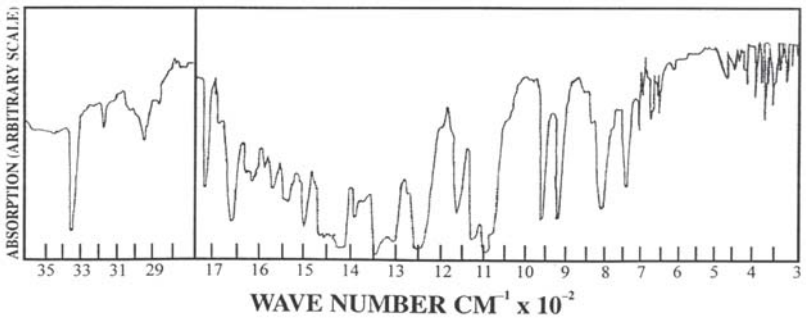

Fig. -2.4: Infrared spectra of $Zn(ETH)_2$-$AgClO_4$ in KBr disc

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