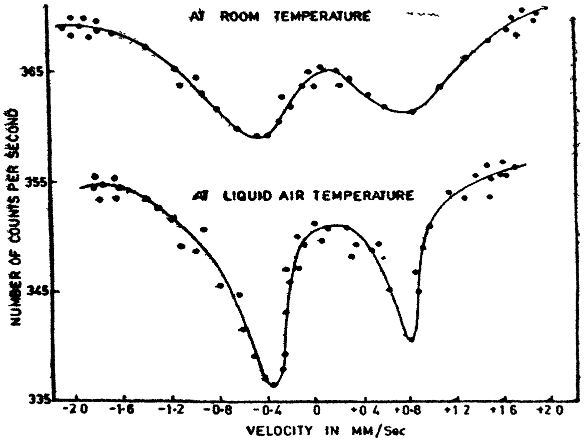

Fig. 1

A comparison of the observed △ value with those of other heavy metal hexacynoferrates(III) indicates an abnormally high value. Moreover △ is temperature independent which is the characteristic of a high spin state. The abnormally high value of △ suggests that all Fe(III) in the complex under investigation may not be in the low spin state and may be partly in the form of polarized Fe^{3+}. This is possible if we assume a resonance of the following type between two structure $Tl[Fe(CN)_6] \leftrightarrows Fe[Tl(CN)_6]$ in which Tl(III) has exchanged with Fe(III) in the coordination sphere. Such an exchange is likely to cause ligand isomerism, since Fe(III) has stronger tendency to bond through C while Thallium(III) prefers nitrogen bonding. Such a resonance having isocyanide structure will result in high distortion of the octahedral symmetry which will consequently increase the quadrupole splitting. It can therefore be safely concluded that there is a possibility of the co-existence of the high spin Fe^{3+} and the low spin Fe(III) in the complex, a conclusion reached earlier on the basis of Magnetic susceptibility measurements in the case of iron (II)-*bis*-(i, 10-phenanthroline)[4]. Moreover, the actual spectrum is an asymmetric doublets due to the superimposition of quadrupole doublets for the low spin Fe(III) and high spin Fe^{3+} and as such high value of △ is observed similar to the case of prussian blue reported by Maer and Beasley[5].

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Cadmium(II) and Mercury(II) Complexes with N-N′-Diphenylthiocarbazide

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COMPLEXES of Zinc, Cadmium and Mercury(II) with sulphur ligands are of considerable interest as potential fungicides. Earlier complexes of substituted thiourea, dithiourea and mixed ligand complexes[1,2] of thiourea and nitrogen bases have been reported. While studying complexes of d^{10} metal ions with sulphur ligands, ligands containing both sulphur and nitrogen donor sites aroused our interest. As a part of this programme, in recent communication, we have reported[3-4] complexes of substituted thiocarbamides of divalent metal ions. In the present communication several Hg(II) and Cd(II) complexes with N-N′-diphenyl thiocarbazide have been described.

Experimental

All the chemicals used are of AnalaR grade.

Synthesis of the ligand : Phenyl hydrazine (5.16 ml) was added slowly into a beaker containing carbondisulphide (2 ml) kept in the freezing mixture when an exothermic reaction took place with the formation of white solid N-N′-diphenyl thiocarbazide. It was then recrystallized from rectified spirit when white crystalline compound separated out which was then filtered, washed with ethanol and dried in vacuum.

Preparation of complexes : Ethanolic solution of metal halides were reacted separately with ethanolic solution of the ligand in 1 : 2 ratio and refluxed for 1 hr. On cooling white crystalline solid complexes separated out which were then filtered, washed with ethanol and dried in vacuum.

Metal, sulfur and nitrogen in the complexes were estimated by standard methods. Conductance was measured in $M/_{1000}$ acetone solution of the complexes using Toshniwal conductivity bridge. IR spectra were recorded in kBr phase using Beckman IR-20 and Perkin-Elmer-621 spectrophotometer. Relevant analytical and spectral data are recorded in Table 1.

Results and Discussion

All the complexes reported in the present investigation have the general composition $[MLX_2]$, where M = Cd(II), Hg(II), X is Cl^-, Br^-, I^-, NO_3^-, SCN^- and L is N-N′-diphenyl thiocarbazide except the perchlorate complex which has the formula $[Cdl_2]\,x_2$. These are white crystalline solids, have relatively low melting points and are soluble in acetone in which medium the Λ_M values are in the range of 8-12 mhos cm^2 indicating non-electrolytic nature of these complexes. Perchlorate complex has

TABLE 1—M.P. ANALYSIS, CONDUCTANCE AND IR SPECTRAL DATA

Compound	M.P. °C	% Metal		% Sulphur		% N		ΔM mhos cm^2	ν(C=S)	ν(NH)	ν(M-S)	ν(M-N)
		Found	Reqd.	Found	Reqd.	Found	Reqd.					
L	150	-	-	12.49	12.28	21.70	21.57	-	1210	3150 3350	-	-
[$HgLCl_2$]	202	37.88	37.43	6.04	5.86	10.57	10.32	8.00	1190	3100 3280	260	350
[$HgLBr_2$]	225	32.43	32.07	5.17	5.04	9.05	8.69	11.5	1185	3120 3250	285	365
[$HgLI_2$]	167	28.15	28.10	4.49	4.31	7.86	7.54	12.00	1190	3130 3255	270	360
[$HgL(NO_3)_2$]	207	34.43	34.19	5.49	5.27	14.40	14.17	9.5	1180	3100 3260	265	380
$HgL(SCN)_2$]	220	34.91	34.58	16.74	16.58	14.74	14.43	10.6	1190	3110 3275	260	375
[$CdLCl_2$]	244	25.47	25.10	7.25	7.07	12.78	12.56	8.9	1185	3100 3265	290	380
[$CdLBr_2$]	252	21.11	20.89	6.03	6.01	15.61	15.29	10.5	1180	3105 3275	260	375
[$CdLI_2$]	240	18.00	17.53	5.08	4.85	8.89	8.57	11.0	1185	3100 3280	270	370
[CdL_2] $(ClO_4)_2$	250(d)	13.58	13.27	7.44	7.58	13.52	13.28	21.2	1185	3100 3270	280	360

L = N-N^1-diphenyl thiocarbazide.

the conductance value 212 mhos cm^2 suggesting 1 : 2 electrolytic nature of this compound.

IR spectra of the ligand and the complexes are quite informative. The ligand has two absorption bands in the 3150 and 3350 cm^{-1} region assignable to ν (N-H), in the 1500-1600 region assignable to δ (NH), a band at 1470 cm^{-1} due to ν (C-N) and at 1210 due to ν (C=S). In addition, it has several bands in the 700-1400 region probably due to coupled C-N and C-S vibrations[5]. In the complexes ν (N-H) is observed $\sim$3100-3280 cm^{-1} (several bands). ν (C-N) $\sim$ 1460 and ν (C=S) $\sim$ 1190 cm^{-1} region. Splitting of ν (N-H) band and decrease of ν (C-N) and ν(C=S) to lower frequency regions provide evidence of bonding through thiocarbonyl sulfur and nitrogen of one of the -NH groups. This has been further substantiated by observation[6] of ν(M-S) and ν(M-N) $\sim$ 260-290 and $\sim$ 350-380 cm^{-1} region.

In the thiocyanato complex ν (C$\equiv$N) is observed at 2130 cm^{-1}. An increase of more than 50 cm^{-1} compared to KNCS indicates the thiocyanato group to be terminally S-banded on the basis of earlier observation[7]. In the nitrato complex the ν_4 (NO_2 asymetric stretch) and ν_1 (NO_2 symmetric stretch) bands are observed at 1400 and 1280 cm^{-1} and the difference ($\Delta\nu$) is 120 cm^{-1} indicating the presence of monodentate nitrato group, in conformity with earlier studies[8-9]. In case of the perchlorate complex, a broad band appears at 1100 cm^{-1}. It is known that co-ordinated perchlorate group shows three distinct bands at 1155, 1080 and 1005 cm^{-1} and ionic perchlorate gives rise to a broad absorption band in the 1060-1150 cm^{-1} region. Hence the perchlorate complex contains ionic perchlorate group in conformity with earlier observations[10] and molar conductance data.

Hence all the Cd(II) and Hg(II) complexes reported in the present investigation presumably have a tetrahedral environment around the metal ions.

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