

Hexamethyleneiminecarbodithioates of Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Pt(II), Co(III), Ru(III), Rh(III) & Ir(III): Synthesis & Structure

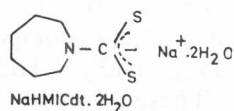
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The complexes of the type $M(\text{HMICdt})_2$ or 3 , where $M = \text{Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Pt(II), Co(III), Ru(III), Rh(III) or Ir(III)}$ and HMICdt^- = hexamethyleneiminecarbodithioate, have been prepared. Their structures have been established by elemental analyses, conductance and magnetic measurements, electronic, IR, ^1H and ^{13}C NMR spectra and X-ray powder patterns. The $M(\text{HMICdt})_3$ type complexes have octahedral geometry. The Ni(II), Pd(II) and Pt(II) complexes have been found to be square planar whereas MS_4 group seems to have a somewhat flattened tetrahedral structure in the case of Zn(II), Cd(II) and Hg(II) . A secondary interaction between the S of a MS_4 group and M of another complex molecule seems to exist in Zn, Cd and Hg complexes. The infrared and NMR have indicated that the CSS^- group is symmetrically chelated with all these metal ions.

The applications of metal dithiocarbamates in diverse areas have attracted many research workers for exploring the chemistry¹⁻³ of such derivatives. Recently we have studied⁴ the ligation of CSS^- group linked to a seven-membered nonplanar saturated heterocyclic ring system (hexamethyleneiminecarbodithioate, HMICdt^-) with some metal ions and observed interesting differences in comparison to those of planar analogues. The stabilization of Mn(II) complex requires auxillary ligand like 1,10-phenanthroline. The polymeric Mn(HMICdt)_2 is unstable in comparison to similar other manganese(II) dithiocarbamates, probably due to steric reasons arising from the nonplanarity of the heterocyclic ring system. In continuation of these studies, the present paper describes the synthesis and structural features of complexes of HMICdt^- with $\text{Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Pt(II), Co(III), Ru(III), Rh(III)}$ and Ir(III) .



Materials and Methods

The ligand was synthesized as described earlier⁴. The complexes were synthesized by the following methods.

Tris(hexamethyleneiminecarbodithioate)cobalt(III)

To a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.8 g) in water (15 ml) was added H_2O_2 (7.6 ml; 30% v/v) with vigorous stirring. The resulting solution was

poured slowly into a slurry of NaHCO_3 (3.4 g) made in a minimum amount of water. The green solution which resulted was set aside for 5 min and an aqueous solution of NaHMICdt (3.8 g) was slowly added to it with stirring. The dark green precipitate formed instantaneously was filtered off, washed thoroughly with distilled water and dried over P_2O_5 in *vacuo*; yield ~ 80%.

Tris(hexamethyleneiminecarbodithioate)ruthenium(III) and -rhodium(III)

A solution of the ligand (6.4 mmol) in water (10 ml) was slowly added to a solution of RhCl_3 or RuCl_3 (2 mmol) in water (10 ml) with constant stirring and heated on a water-bath for 1 hr. The resulting brown precipitate was filtered, washed thoroughly with aq methanol (1:2) and dried over P_2O_5 in *vacuo*; yield ~ 65-70%.

Tris(hexamethyleneiminecarbodithioate)iridium(III)

A solution of IrCl_3 (2 mmol) in 1:2 aq methanol (10 ml) was mixed with the ligand (6 mmol) dissolved in a minimum amount of water, with constant stirring. The mixture was refluxed for 3 hr, the resulting brown precipitate filtered, washed thoroughly with aq methanol (1:2) and dried over P_2O_5 in *vacuo*; yield ~ 70%.

Bis(hexamethyleneiminecarbodithioate)nickel(II), -zinc(II), -cadmium(II) and -mercury(II)

All these metal chelates were prepared by reacting the corresponding metal dichloride (0.25 g) with NaHMICdt in 1:2 (metal:ligand) molar ratio in a minimum amount of water. The com-

Table 1 – Characterization Data of Complexes

Complex	Colour	m.p. (°C)	Found (Calc.), (%)			
			Metal*	C	H	N
Ni(HMICdt) ₂	Yellowish green	249	14.53 (14.41)	42.50 (41.28)	5.90 (5.94)	7.10 (6.88)
Zn(HMICdt) ₂	White	165	15.86 (15.79)	41.50 (40.62)	6.19 (5.84)	6.60 (6.77)
Cd(HMICdt) ₂	White	231	24.00 (24.38)	35.81 (36.48)	5.41 (5.25)	5.90 (6.07)
Hg(HMICdt) ₂	Greenish yellow	188	36.30 (36.52)	30.00 (30.62)	4.30 (4.40)	5.00 (5.10)
Pd(HMICdt) ₂	Yellow	240	22.80 (22.38)	37.51 (39.96)	5.50 (5.32)	6.00 (6.16)
Pt(HMICdt) ₂	Yellow	> 250	35.50 (35.88)	31.60 (30.93)	4.30 (4.45)	5.32 (5.15)
Co(HMICdt) ₃	Green	> 250	10.50 (10.13)	44.40 (43.35)	6.50 (6.24)	7.15 (7.22)
Ru(HMICdt) ₃	Black	230	16.50 (16.20)	41.30 (40.44)	6.00 (5.77)	6.52 (6.73)
Rh(HMICdt) ₃	Orange-red	> 250	16.00 (16.44)	39.20 (40.30)	5.90 (5.80)	6.50 (6.71)
Ir(HMICdt) ₃	Brown	> 250	26.06 (26.88)	34.58 (35.27)	5.20 (5.07)	5.98 (5.86)

*Metal contents were determined by atomic absorption spectroscopy after decomposing the complexes with conc. HNO₃.

plexes which precipitated out immediately were filtered off, washed repeatedly with cold distilled water and finally dried over P₂O₅ *in vacuo*; yield ~ 75-85%.

Bis(hexamethyleneiminecarbodithioate)palladium (II) and -platinum(II)

A solution of PdCl₂ or PtCl₂ (2 mmol) in water (10 ml) was slowly added to a solution of the ligand (6.4 mmol) in a minimum amount of water. The mixture was stirred for 1 hr, the resulting precipitate filtered, washed thoroughly with distilled water and dried over P₂O₅ *in vacuo*; yield ~ 75-80%.

Spectral, magnetic susceptibility, conductance and X-ray measurements and thermal analyses

The IR spectra in the range 4000-200 cm⁻¹ were recorded in CsI on Perkin-Elmer 580 B and Nicolet 5DX FT-IR spectrophotometers. Electronic spectra in nujol and chloroform were recorded on 554 Perkin-Elmer and Hitachi 330 UV-VIS spectrophotometers. ¹H and ¹³CNMR spectra were recorded on a Jeol JNM-FX 100 FT NMR in DMSO-*d*₆ at 27°C using TMS as an internal standard.

Magnetic susceptibilities were measured on a PARC model 155 vibrating sample magnetometer. The conductance measurements were carried out on a W.G. Pye conductance bridge. A DuPont

1090 thermal analyzer having a 951 TGA module was used to study the thermal decomposition patterns at a heating rate of 10°C/min under N₂ atmosphere. Powder diffraction patterns were obtained on a Philips PW 1140/90 X-ray diffractometer, at goniometer speed of 1°/min, using nickel-filtered copper K_α radiation (λ = 1.5405 Å).

Results and Discussion

The results of elemental analyses, recorded in Table 1, authenticate the assigned stoichiometries. All the complexes behaved as nonelectrolytes in nitrobenzene as expected. All of the complexes decomposed in one step between 200 and 600°C, except Hg(II) complex for which the second step closely following the first one was also observed. The residues left had the compositions CoS_{2.5}, NiS, ZnS_{1.5}, CdS_{3.5}, HgS_{2.8}, PdS, PtS, RuS_{2.7}, RhS_{2.5} and IrS_{2.8}. These observations further support the stoichiometries assigned to the complexes and also indicate that metal-ligand interaction is through sulphur only.

The electronic spectrum of the diamagnetic Ni(HMICdt)₂ in CHCl₃ exhibited two *d-d* bands; the lowest energy band at 15.87 kK may be assigned to ¹A_{1g} → ¹B_{1g} transition and the next higher at 21.05 kK to ¹A_{1g} → ¹B_{3g}, suggesting a square planar arrangement of donor atoms around nickel. The bands at 23.26, 25.84 and 30.30 kK

Table 2 – NMR Chemical Shifts (δ , ppm) of the Complexes in DMSO- d_6 Using TMS as an Internal Standard

Complex	^1H			^{13}C			
	$\alpha\text{-CH}_2$	$\beta\text{-CH}_2$	$\gamma\text{-CH}_2$	C- α	C- β	C- γ	CSS $^-$
(HMICDdtNa).2H $_2$ O	4.12(t)	1.68(m)	1.46(m)	53.52	27.29	26.56	212.15
Ni(HMICdt) $_2$	3.74(m)	1.74(m)	1.52(m)	48.17	27.20	26.56	206.51
Zn(HMICdt) $_2$	3.96(t)	1.75(m)	1.54(m)	54.84	26.49	26.19	203.00
Cd(HMICdt) $_2$	3.98(t)	1.75(m)	1.52(t)	55.21	25.61	25.24	205.55
Hg(HMICdt) $_2$	3.94(t)	1.78(m)	1.56(m)	57.48	26.27	26.05	201.66
Pd(HMICdt) $_2$	3.85(t)	1.85(m)	1.63(m)	49.67	27.15	26.66	207.12
Pt(HMICdt) $_2$	3.78(t)	1.92(m)	1.66(m)	48.65	27.25	26.46	206.12
Co(HMICdt) $_3$	3.67(t)	1.74(m)	1.52(m)	49.27	27.38	26.37	206.42
Rh(HMICdt) $_3$	3.83(t)	1.82(m)	1.57(m)	48.35	27.15	26.70	207.45
Ir(HMICdt) $_3$	3.77(t)	1.83(m)	1.61(m)	47.91	27.10	26.60	206.15

seemed to be due to metal-ligand charge transfer. The value of Δ_1 for this nickel complex was found to be 18.80, placing the ligand in the spectrochemical series of sulphur donors⁵ in the same position as diethyldithiocarbamate. The nature and extent of shift observed in $\nu(\text{C}\equiv\text{N})$, $\nu_s(\text{C}\equiv\text{S})$ and $\nu_{as}(\text{C}\equiv\text{S})$ on complexation were of the same order of magnitude as reported in the literature⁶, indicating symmetric bonding of the diethiocarbamate group. The $\nu(\text{Ni}-\text{S})$ mode appeared at 394 cm^{-1} . To get further insight of the bonding of bisulphur fork of HMICdt $^-$ with the nickel ^1H and ^{13}C NMR of the ligand and its Ni(II) complex were studied (Table 2). In the PMR of the ligand $\alpha\text{-CH}_2$ protons appeared as a triplet at δ 4.12 ppm. In the Ni complex this signal was shielded and appeared at δ 3.74 ppm. However, no change in the fine structure of this triplet was noticed. This suggests that on complexation the lone pair on nitrogen is further drifted towards carbon of CSS $^-$ group, giving more double bond character to C–N bond, which due to its anisotropic effect shields the $\alpha\text{-CH}_2$ protons. Such a behaviour is possible only when CSS $^-$ group coordinates symmetrically as a bidentate ligand. Moreover, the γ - and $\beta\text{-CH}_2$ protons of the ligand which appeared at δ 1.46(m) and 1.68(m) ppm respectively were found to be a little bit deshielded (~ 0.06 ppm) in the complexes, further supporting symmetrical bonding of the ligand. In ^{13}C NMR spectrum of the ligand the CSS $^-$ carbon, which appeared at δ 212.15 ppm was shielded by ~ 6 ppm in the Ni(II) complex. The signal due to C- α also underwent upfield shift from δ 53.52 ppm in the ligand to 48.17 ppm in the complex. These observations in conjunction with the negligible effects on signals due to β and γ carbons on complexation, further support the inference that the bisulphur fork is symmetrically bonded to metal.

The IR spectra of Zn(HMICdt) $_2$, Cd(HMICdt) $_2$ and Hg(HMICdt) $_2$ exhibited two $\nu(\text{M}-\text{S})$ modes between 390 and 300 cm^{-1} , suggesting the formation of two types of metal-sulphur bonds in these complexes. In comparison to Ni(HMICdt) $_2$, these complexes exhibited an additional $\nu_{as}(\text{C}\equiv\text{S})$ mode around 960 cm^{-1} . The ^1H NMR spectra of these complexes were similar to that of the nickel complex. However, ^{13}C NMR spectra (Table 2) revealed that the signals due to β and γ -carbon atoms were shielded, C- α signal was deshielded and the CSS $^-$ carbon underwent upfield shift. These observations suggest that some sulphur atoms of the MS $_4$ group are involved in an interaction other than the one resulting in a four-membered chelate ring. Therefore, MS $_4$ group does not have the expected regular tetrahedral structure. To understand the distortion the X-ray powder patterns of zinc, cadmium and mercury complexes were compared with the powder pattern of copper complex which in all probability has a square planar structure⁴. The four chelates were found to be isomorphous, suggesting that the four sulphur atoms in Zn(II), Cd(II) and Hg(II) complexes are at the four corners of a virtually flattened tetrahedron. Moreover, a moderate to strong interaction of the type S $_3$ MS $_4$MS $_4$ seems to exist in these complexes, at least in solid state. However, in view of the solubility, the possibility of their existence as a chain type coordination polymers is ruled out.

The electronic spectra of the diamagnetic Pd(HMICdt) $_2$ and Pt(HMICdt) $_2$ in chloroform displayed bands at 22.22, 28.99 and 33.11 kK and 25.00, 28.99 and 37.74 kK respectively. Of these the first one may be assigned to spin allowed $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ transition expected for a square planar complex. The bands around 29 kK seem to be of charge transfer origin. The bands at 33.11 and

37.74 kK can be ascribed to intraligand transitions. The $\Delta_1 = \nu_1 + 3.5F_2$, where $F_2 = 10F_4 = 0.6$ kK is the Slater-Condon interelectronic repulsion parameter, has been found to be 24.32 and 27.10 kK respectively for Pd and Pt complexes. The $\nu(\text{Pd}-\text{S})$ and $\nu(\text{Pt}-\text{S})$ were observed at 378 and 358 cm^{-1} respectively. The nature and extent of shift of $\nu(\text{C}\equiv\text{N})$, $\nu_s(\text{C}\equiv\text{S})$ and $\nu_{as}(\text{C}\equiv\text{S})$ modes suggest that the bisulphur fork is chelated to Pd or Pt in a manner analogous to that of Ni(II). In the PMR spectra of Pd and Pt complexes (Table 2) $\alpha\text{-CH}_2$ protons were shielded while β - and $\gamma\text{-CH}_2$ protons were deshielded as in the case of Ni(II) complex, supporting the symmetrical chelation of CSS^- group.

The electronic spectrum of diamagnetic $\text{Co}(\text{HMICdt})_3$ exhibited bands at 15.63, 20.62, 25.00, 27.78, 30.77 and 35.71 kK. The first two of these may be assigned to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ transitions respectively, arising from octahedral cobalt(III). The absorptions at 25, 27.78 and 30.77 kK may be attributed to metal-ligand charge transfer while the one at 35.71 kK is due to intraligand transition. The 10 Dq, B, β and LFSE have been found to be 16.97 kK, 0.336 kK, 0.30 and 489 kJ mol^{-1} respectively. The lower values of β suggest strong covalent nature of Co-S bond, which causes extensive delocalization of the antibonding e_g electrons onto the ligand. The value of 10 Dq indicates that HMICdt^- produces a weak ligand field. The covalency of Co-S bond is further supported by low value (0.25) of the parameter 'z'. The $\nu(\text{Co}-\text{S})$ in the IR spectrum of the Co(III) complex was observed at 392 cm^{-1} . The ^1H and ^{13}C NMR spectra (Table 2) and the other IR bands of $\text{Co}(\text{HMICdt})_3$ were almost identical to those of Ni(II) complex, suggesting symmetrical chelation of Co(III) by the bisulphur fork.

The μ_{eff} of $\text{Ru}(\text{HMICdt})_3$ was found to be 1.88 B.M. as expected for an octahedral complex with t_{2g}^5 configuration. Its electronic spectrum in chloroform displayed bands at 17.86, 21.51, 27.78 and 33.90 kK, which may be assigned to $^2\text{T}_{2g} \rightarrow ^4\text{T}_{1g}$,

$^2\text{T}_{2g} \rightarrow ^4\text{T}_{2g}$, $^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$, $^2\text{T}_{1g}$ and charge transfer respectively. The low value (0.456) for B indicates that Ru-S bond has significant covalency. This is further supported by the value of 'z' which was found to be 0.96. The $\nu(\text{Ru}-\text{S})$ in the IR spectrum was observed at 380 cm^{-1} .

The electronic spectrum of diamagnetic $\text{Rh}(\text{HMICdt})_3$ in chloroform exhibited bands at 22.86, 32.05 and 39.06 kK as expected for a low spin octahedral d^6 -system. The last two bands have quite high value of ϵ , indicating their charge transfer nature. The first one may be assigned to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition. The $\nu(\text{Rh}-\text{S})$ band in the IR spectrum was observed at 386 cm^{-1} .

The electronic spectrum of the diamagnetic $\text{Ir}(\text{HMICdt})_3$ in chloroform displayed bands at 24.10, 28.17, 34.48 and 37.74 kK, which can be assigned to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$, $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$, charge transfer and intraligand transitions respectively. These observations also suggest the octahedral arrangement of sulphur atoms around iridium in IrS_6 . The values of B, β and 'z' have been found to be 0.27 kK, 0.41 and 0.17 respectively, suggesting significant covalency in Ir-S bond. The $\nu(\text{Ir}-\text{S})$ in the IR spectrum was observed at 365 cm^{-1} . The nature and extent of shift of $\nu(\text{C}-\text{N})$, $\nu_s(\text{C}\equiv\text{S})$ and $\nu_{as}(\text{C}\equiv\text{S})$ modes in the IR spectra of $\text{Ru}(\text{HMICdt})_3$, $\text{Rh}(\text{HMICdt})_3$ and $\text{Ir}(\text{HMICdt})_3$ favour symmetric chelation of CSS^- group in these complexes as in the case of Ni(II) complex. Additional support to this chelation was provided by the ^1H and ^{13}C NMR spectra (Table 2) of Rh and Ir complexes.

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