Inorganica Chimica Acta, *132* (1987) 33–36

^1H and ^{13}C NMR Study of Hydantoin Complexes with Antimony, Cadmium and Mercuric Chlorides

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(Received December 10, 1986)

Abstract

Hydantoin complexes with antimony(V), cadmium(II), and mercuric chlorides were synthesized. Antimony and cadmium complexes were found to involve solvent (MeOH) in their formation while this behaviour was not observed with mercury complexes. The complexes were studied by ^1H and ^{13}C NMR spectroscopy and the chemical shifts are reported.

Introduction

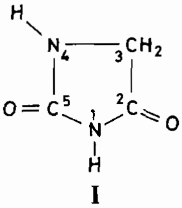
After the cadmium and mercury poisoning in Japan in the 1970s, heavy metals as potential hazards have been the most investigated pollutants in aquatic systems [1, 2]. The effect on human life was attributed to the methylmercury ion ($MeHg^+$) which causes irreversible complex disturbances of the central nervous systems [3–5]. The evolution of the concentration of the heavy metals, mainly Cd, Zn, Cu, Pb and Hg, in aquatic sediments runs parallel to world-wide industrialization and creates more interest in heavy metal complexes [6, 7].

We devoted this study to the elucidation of the nature of hydantoin complexes with $SbCl_5$, $CdCl_2$ and $HgCl_2$ in an attempt to illuminate the potential of these compounds. Hydantoin was chosen for this study for the following reasons: (i) hydantoin complexes are similar to thiazolidine derivatives complexes which are of great interest both structurally and pharmacologically [8, 9]; (ii) hydantoin contains different sites of coordination and the donor ability towards metal ions makes it a good ligand in coordination compounds [10, 11]; (iii) the ^{13}C NMR spectrum has three signals which resonate at characteristic regions.

There is considerable current interest in the NMR spectra of organometallic compounds and related complexes. It was hoped that the present study would increase the understanding of the nature of these complexes and the factors governing the NMR parameters.

Results and Discussion

During the course of this investigation, hydantoin complexes with antimony(V), cadmium(II) and mercury(II) chlorides were synthesized and their ^1H and ^{13}C NMR spectra are reported for the first time (Tables I and II). The ^1H NMR spectrum of hydantoin (I) in DMSO-d_6 shows three signals at 3.35, 3.84 and 6.68 δ attributed to CH_2–*NH*, $CH_2-\overset{O}{\overset{/\!/}{C}}$ and $-\overset{O}{\overset{/\!/}{C}}-NH-\overset{O}{\overset{/\!/}{C}}$ protons respectively The ^{13}C NMR spectrum of the free hydantoin in DMSO-d_6 solution showed three signals at 173.84, 158.34 and 47.20δ which were assigned to C-2 C-5 and C-3 respectively.



I

TABLE I. ^1H NMR Data in DMSO-d_6 at 28 °C[a]

	3-CH_2	1-NH	4-NH[b]	Others[c]
Free hydantoin	3.84	7.68	3.35	
Hydantoin–$SbCl_5$	3.84	7.65	3.33	3.19, 4.33
Hydantoin–$CdCl_2$	3.83	7.67	3.33	3.14, 4.33
Hydantoin–$HgCl_2$	3.84	7.69	3.39	

[a]Chemical shifts in ppm δ relative to TMS. [b]For numbering see I in the text. [c]The Me and OH signals of MeOH respectively.

TABLE II. ^{13}C NMR Data in DMSO-d_6 at 28 °C[a]

	C-2	C-3	C-5[b]	Others[c]
Free hydantoin	173.84	158.34	47.34	
Hydantoin–$SbCl_5$	173.80	158.30	47.26	46.90
Hydantoin–$CdCl_2$	173.70	158.20	48.60	47.30
Hydantoin–$HgCl_2$	173.61	158.11	47.09	

[a]Chemical shifts in ppm δ relative to TMS. [b]For numbering see I in the text. [c]The Me signal of MeOH.

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Hydantoin with $SbCl_5$, $CdCl_2$ and $HgCl_2$ in methanol at room temperature was found to be unreactive, however, reflux for a few hours lead to a precipitate of the relative complexes. There is no evidence in the literature about these specific reactions, but similar reactions of nitrogen compounds (e.g. ammonia and amines) with metal chlorides have been reported. For example, there are three known products of the reaction of $HgCl_2$ with ammonia; the proportion of any one of them depends on the conditions of the reaction [3] (eqns. (1)–(3))

$$HgCl_2 + 2NH_3 \rightleftharpoons Hg(NH_3)_2Cl_2(s) \tag{1}$$

$$HgCl_2 + 2NH_3 \rightleftharpoons HgNH_2Cl(s) + \overset{+}{N}H_4 + 3Cl^- \tag{2}$$

$$2HgCl_2 + 4NH_3 + H_2O \rightleftharpoons Hg_2NCl{\cdot}H_2O + 3\overset{+}{N}H_4 + 3Cl^- \tag{3}$$

Another example comes from the reaction of $BiCl_3$ with aliphatic and aromatic amines to give the corresponding complexes [12], eqn. (4).

$$BiCl_3 + R{-}NH_2 \rightleftharpoons [R\overset{+}{N}H_2BiCl_2]Cl^- \tag{4}$$

There are several ^1H NMR investigations of amides and substituted urea adducts where the question of O *versus* N-coordination has been discussed [13]. The present data obtained from ^1H NMR (Table I); ^{13}C NMR (Table II) and microanalytical data indicate that $SbCl_5$ and $CdCl_2$ behave similarly to form hydantoin complexes under similar conditions.

The reaction of hydantoin with $SbCl_5$ lead to a yellow precipitate which changed to a white precipitate after drying. Microanalysis indicated that four molecules of hydantoin were used as ligands, eqn. (5).

$$\begin{aligned} SbCl_5 + 4L + MeOH &\rightleftharpoons SbCl_4(L{\cdot}HCl){\cdot}MeOH{\cdot}HCl \\ &\quad \text{or } SbCl_5{\cdot}4LH{\cdot}MeOH{\cdot}HCl \end{aligned} \tag{5}$$

where L = hydantoin.

Under similar conditions, the reaction of $CdCl_2$ with hydantoin involves one molecule of hydantoin and two molecules of methanol, eqn. (6).

$$3CdCl_2 + L + 2MeOH \rightleftharpoons 3CdCl_2{\cdot}L{\cdot}2MeOH \tag{6}$$

The ^1H NMR spectra indicated the presence of MeOH, the two signals appearing at 3.14 and 4.33 δ being attributed to the methyl and hydroxyl protons respectively. Further evidence confirming incorporation of the solvent comes from the ^{13}C spectra where the methyl ^{13}C signal of the methanol resonates at 47.30δ. Solvent incorporation in complex formation is well demonstrated in the literature [3, 14]. Solvents such as methanol, dimethylformamide and acetonitrile have been found capable of adding to metal complexes [3, 14]. Recently, $SbCl_3$ complexes such as: $SbCl_2[CON(CH_3)_2]{\cdot}(C_2H_5)_3N$; $SbCl_2[CON(CH_3)_2]{\cdot}(C_2H_5)_2NH$ and $SbCl_2[CON(CH_3)_2]{\cdot}HOCON(CH_3)_2$ were reported containing the solvent acetonitrile [15].

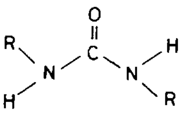
The reaction of $HgCl_2$ with hydantoin was found to follow eqn. (7)

$$HgCl_2 + 2L \rightleftharpoons HgCl_2L_2 \tag{7}$$

The ^1H NMR spectra revealed the presence of NH protons (Table II). Incorporation of the solvent has not been observed in the formation of these mercury complexes.

The ^{13}C NMR data available in the literature for organometallic compounds indicate that numerous trends have been noted in ^{13}C chemical shifts [16]. Several attempts have been made to correlate the ^{13}C parameters with other constants [17]. The literature data suggest that the polarizability of the metal (gold, silver, platinum, mercury and copper) makes changes in the charge distribution of the metal in the $^{13}C{-}M{-}X$ fragment causing major changes in the shielding of the ^{13}C shifts [17].

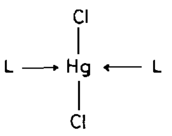
The ^{13}C NMR data in the present study (Table II) indicate that the shielding of the $^{13}C{-}N$ chemical shifts remained unchanged compared to the mother molecule (hydantoin). This behaviour may be due to the weak degree of polarizability of the $^{13}C{-}N{-}M$ bonds. These results suggest that coordination takes place on the nitrogen atoms of hydantoin while the carbonyl groups remained unaffected. There is evidence in the literature that in the case of alkyl substituted ureas of the type **II** based on the chemical reactions, N-coordination was observed in boron trichloride and PCl_5 adducts [13].



II

We believe that hydantoin complexes occur utilizing the lone pair of nitrogen electrons. Investigation of the electronic configuration of $HgCl_2$, $CdCl_2$ and $SbCl_5$ indicates that dative bonds can be formed between the metal and the lone pair of nitrogen electrons to form these complexes where sp hybridization is available [18].

The following structures are suggested for the complexes:



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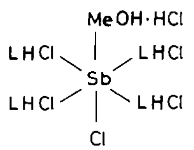
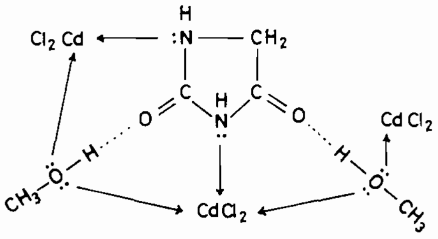


IV



V

There are support evidences from mass spectra fragmentation for the above structures for example, *m/e* = 100 for hydantoin ligand, *m/e* = 36 for HCl, *m/e* = 32 and 31 for MeOH and MeO respectively, *m/e* = 57 for $\mathrm{CH_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}NH}$ or $\mathrm{N{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}NH}$ and all other fragments such as Sb, SbCl, $SbCl_2$, $SbCl_3$ and $SbCl_2$• hydantoin, Cd, CdCl, $CdCl_2$ and $CdCl_2$•LH•CH_3OH are also present in the mass spectra of $SbCl_5$ and $CdCl_2$ hydantoin complexes.

Conclusion

From the spectroscopic data. ^1H, ^{13}C NMR, mass spectra and elemental analysis, it is clear that $SbCl_5$ and $CdCl_2$ with hydantoin form complexes of the formula SbCl•4LHCl•MeOH•HCl and $3CdCl_2$•L•2MeOH respectively, where the solvent MeOH is also coordinated. $HgCl_2$ on the other hand, forms the complex $HgCl_2L_2$. The suggested structures given agree with the proposed formula.

Experimental

Hydantoin, $SbCl_5$, $CdCl_2$ and $HgCl_2$ were anhydrous analar chemicals and all the solvents were pure. Elemental analyses were carried out by Mikroanalytisches Labor Pascher-Bonn, F.R.G. by addition of V_2O_5 to all C, H, N and Cl combustion. Some halogens were determined by ion chromatography.

NMR Spectra [19]

^1H NMR spectra

^1H observe frequency 100 MHz; pulse width 20 μs (45°); pulse delay auto set, acquisition time auto set, data points 8k; spectral width 1000 Hz; effective resolution 0.10 Hz, probe temperature 28 °C, sample tubes 10 mm, probe $^1H/^{13}C$ dual probe and deuterium internal lock.

^{13}C NMR spectra

^{13}C observe frequency 25 MHz; pulse width 10 μs (45°); pulse delay 15 s, acquisition time auto set; data points 8k; spectral width 5000 Hz, effective resolution 0.05 ppm, sample tube 10 mm; probe $^1H/^{13}C$ dual probe, ^1H noise decoupling and internal lock of the deuterium signal of the solvent.

Mass Spectra

Mass spectra were recorded at 70 eV on an AEIMS-30 double beam mass spectrometer by Mikroanalytisches Labor Pascher, Bonn, F.R.G.

Hydantoin Complexes

All reactions were carried out under a nitrogen atmosphere in a three-necked flask equipped with magnetic stirrer, condenser and N_2 inlet. To a hot solution of hydantoin (0.01 mol) in methanol (25 ml) a solution of $SbCl_5$, $CdCl_2$ or $HgCl_2$ (0.01 mol) in methanol (20 ml) was added dropwise over a period of 30 min. The reaction mixtures were then refluxed for 3 h with stirring, giving the corresponding hydantoin–metal chloride complexes as follow:

Hexachloro tetrahydantoino hydrochloride•MeOH antimony V

Melting point (m.p.) 195 °C, crystallizes from methanol. Calc. for SbCl•4(hydantoinohydrochloride) MeOH•HCl[$C_{13}H_{25}N_8O_9Cl_6Sb$], M_r = 771.75: C 20.21; H 3.23; N 14.5 O 18.66; Cl 27.60 and Sb 15.78%. Found: C, 19.26; H, 3.17; N, 13.17; O, 17.80; Cl 27.1; Sb 15.90%.

Hydantoin–$CdCl_2$•MeOH complex

m.p. 280 °C, crystallizes from methanol. Calc. for [$C_5H_{12}N_2O_4Cl_6Cd_3$], M_r = 714.109: C, 8.41; H, 1.69; N, 3.92; O, 8.96, Cl, 29.79 and Cd, 47.22. Found: C, 8.15; H, 2.03; N, 1.95; O, 10.70; Cl, 29.20; Cd, 47.80%.

Hydantoin–$HgCl_2$ complex

m.p. 185 °C, crystallizes from methanol. Calc. for [$C_6H_8N_4O_4HgCl_2$], M_r = 471.648: C, 15.28; H, 1.71; N, 11.88; O, 13.57; Hg, 42.53; Cl, 15.03. Found: C, 15.05; H, 1.53; N, 11.30; Cl, 14.80%.

Acknowledgements

The authors would like to thank Mr. M. Gopal for running the NMR spectra, Mr. M. Mukhalalati for technical assistance and King Saud University for financial support.

References

1 U. Förstner and G Müller, 'Schwermetalle in Flüssen und Seen als Ausdruck der Umweltschmutzung', Springer, Berlin/Heidelberg/New York, 1974.
2 L. T. Friberg and J. J. Vostal, 'Mercury in the Environment', CRC Press, Florida, 1972.
3 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 4th edn., Wiley, New York, 1980.

4 L. Rabenstein, *J. Chem. Educ.*, *55*, 292 (1978).

5 K. K. Bertine and E. D. Goldberg, *Science*, *173*, 233 (1971).

6 G. Müller, G. Grimmer and H. Böhnke, *Naturwissenschaften*, *64*, 427 (1977).

7 U. Förstner and G. Müller, *Geoforum*, *14*, 53 (1973).

8 L. S. Goodman and A. Gilman, 'The Pharmacological Basis of Therapeutics', 5th edn., Macmillan, New York, 1975.

9 S. H. Gerson, S. D. Worley, N. Bodor, J. J. Kaminsky and T. W. Flechtner, *J. Electr. Spectrosc. Relat. Phenom.*, *13*, 421 (1978).

10 E. Walker, K. Folting and L. L. Merritt, Jr., *Acta Crystallogr., Sect. B*, *25*, 88 (1969).

11 M. Cannas, G. Carta, G. Marongiu and E. F. Trogu, *Acta Crystallogr., Sect. B*, *30*, 2252 (1974).

12 A. A. Wassil, R. Abu-Samn and M. Mukhalalati, *Inorg. Chim. Acta*, *127*, 5 (1987).

13 P. Stilbs, *Tetrahedron Lett.*, 227 (1972).

14 F. W. A. Fowles, D. J. Tidmarsh and S. A. Walton, *J. Chem. Soc. A*, 1546 (1983).

15 A. K. Mishra, K. N. Tandon and R. G. Mishra, *J. Indian Chem. Soc.*, *LX*, 617 (1983).

16 N. K. Wilson, R. D. Zehr and P. D. Ellis, *J. Magn. Reson.*, *21*, 437 (1976).

17 O. M. Abu-Salah, A. A. Al-Ohaly, S. S. Al-Showiman and I. M. Al-Najjar, *Transition Met. Chem.*, *10*, 207 (1985).

18 N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements', Pergamon, London, 1984.

19 S. S. Al-Showiman, I. M. Al-Najjar and H. B. Amin, *Org. Magn. Reson.*, *20*, 105 (1982).