sodium hydroxide solution. The complexes were separated on addition of alcohol under constant stirring. The molar conductance values of the complexes showed that all of them exhibit electrolytic behavior in water and are in accordance with 2:1 electrolytes. The complex Na$\{UO_2ATPH\}\cdot 4H_2O$ was insoluble in water and all other common organic solvents. In the pure $Na_2H_2ATP\cdot 3H_2O$ the band around 1720 cm^{-1} is attributed to the protonated form of the adenine moiety.

This band, however, is strongly pH dependent and shifts to 1650 cm^{-1} in ATP^{4-} attributable to the non protonated form of the adenine moiety [3]. In all complexes prepared except Na$\{UO_2ATPH\}\cdot 4H_2O$ the infrared spectra in that region showed a strong band around 1650 cm^{-1} indicating that the adenine moiety of ATP is in its nonprotonated form. In these cases there is probably coordination of the metal ion through the N-7 of the purine ring. The ^1H and ^{13}C NMR spectra of the complexes with diamagnetic metal ions also verify these results [4]. The presence of a strong band around 980 cm^{-1} along with changes in intensity and/or frequency in the region between 1300–900 cm^{-1} where the P–O vibrations occur [5], establish that except for the mercury complex, in all other complexes the metal ions coordinate also through the phosphate group of adenosine-5′-triphosphate.

1 A. T. Tu and M. J. Heller in 'Metal Ions in Biological Systems', Vol. 1, H. Sigel Ed., M. Dekker, New York (1979).
2 R. G. Bhattacharyya and J. Bhaduri, *J. Inorg. Nucl. Chem.*, *40*, 733 (1978).
3 F. L. Khalil and T. L. Brown, *J. Am. Chem. Soc.*, *86*, 513 (1964).
4 J. L. Bock, *J. Inorg. Biochem.*, *12*, 119 (1980).
5 M. Tsuboi, *J. Am. Chem. Soc.*, *79*, 1351 (1957).

T8

Multinuclear NMR Studies on $ZnCl_2$–, $CdCl_2$– and $HgCl_2$–Interactions with Adenosin and Guanosin and Other Nitrogen-Heterocycles

MARTIN SCHUMACHER, KLAUS FINNEISER and HARALD GÜNTHER

Fachbereich 8, Organic Chemistry, University of Siegen, Siegen, F.R.G.

^{13}C NMR investigations of nitrogen heterocycles have been established as a useful tool for the detection of protonation sites [1]. The ^{13}C, ^1H spin–spin interactions are particularly sensitive parameters for this purpose, as was shown recently for purine [2]. Even more direct information is available from ^{15}N NMR studies, where chemical shifts are strongly affected by protonation [3, 4].

An extension of such studies to interactions between metal salts and nitrogen heterocycles seemed of interest. The present communication deals with results of ^{13}C, ^{15}N, ^{199}Hg, and ^{113}Cd NMR investigations of adenosin and guanosin in the presence of $ZnCl_2$, $CdCl_2$, and $HgCl_2$ in DMSO-d_6. The information extracted from the various NMR parameters, in particular, ^{13}C,^1H spin–spin coupling constants and ^{15}N as well as ^{199}Hg, and ^{113}Cd chemical shifts is compared, and the contact sites as well as the strength of the interactions are discussed. Similar studies with imidazole and 1-methyl imidazole as well as with purine and its methyl derivatives are described.

1 H. Günther, A. Gronenborn, U. Ewers and H. Seel, in 'NMR in Molecular Biology', B. Pullman (ed.), Reidel, Dordrecht, Holland (1978).
2 M. Schumacher and H. Günther, *J. Am. Chem. Soc.*, *104*, 4167 (1982).
3 N. C. Gonella and J. D. Roberts, *J. Am. Chem. Soc.*, *104*, 3162 (1982).
4 M. Schumacher and H. Günther, *Chem. Ber.*, in print.

T9

Properties and Structure of Pt(II) Complexes with Adenine and Guanine

I. I. VOLCHENSKOVA, N. N. MAIDANEVICH and L. I. BUDARIN

The L. V. Pisarzhevsky Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences, Kiev, U.S.S.R.

The electroneutral *cis*-dichloro complexes of Pt(II) with DNA purine bases are potential chemotherapeutic agents. Therefore, it was necessary to study their properties and structure. In solving the problem one can also elucidate the effect of the metal ions, introduced into a living body, on the biological action of nucleic acids and their monomeric units. Metal complexes with guanine (Gu) are of special interest as a Gu base is the most reactive fragment of DNA with which both chemical cancer agents and Pt(II) antitumour drugs interact selectively.

The physico-chemical properties and structure of the electroneutral complexes of Pt(II) with adenine (Ad) and Gu obtained by mixing aqueous-acidic solutions of the ligands and the metal salt, K_2PtCl_4, (1:1 mole ratio) were studied. Complexes of the type $PtCl_2L(H_2O)_n$ were synthesized, where L = Ad or Gu, n = 0, 1, 2, 3. The complexes with n = 3 dissolve in DMFA and DMSO and the solutions obtained are practically nonconductors of current and are storage stable. The UV spectra (DMSO) are characterized by the intraligand bands of a charge transfer for $PtCl_2$-$Ad(H_2O)_3$ (I) $\nu = 273$ nm, $\epsilon = 10000$ l mol^{-1} cm^{-1},