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.

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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.

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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 $PtCl_2Ad(H_2O)_3$ (I) $\nu = 273$ nm, $\epsilon = 10000$ l mol^{-1} cm^{-1},

for $PtCl_2Gu(H_2O)_3$ (II) $\nu = 278$ nm, $\epsilon = 9200$ l mol^{-1} cm^{-1}.

The $PtCl_2L(H_2O)_n$ complexes have a *cis*-structure as shown by the characteristic IR spectral bands corresponding to the Pt–Cl stretching vibrations at 320 and 338 cm^{-1} and the formation of a $Pt(thio)_4Cl_2$ complex by the reaction with thiourea, specific to *cis*-compounds. IR spectroscopic and thermogravimetric data have revealed that $PtCl_2L(H_2O)_3$ complexes contain H_2O molecules of different types: (I) - only crystal H_2O, (II) - two crystal H_2O molecules and a molecule of coordinated H_2O. The dehydrated complexes were found not to dissolve in known solvents, strong acids and alkalis. The IR spectra of $PtCl_2L(H_2O)_n$ with different n and the complexes with deuterated L at 1500–1700 and 3100–3500 cm^{-1} (vaseline oil) indicate that both bases interact with Pt^+ ions only *via* the purine heterocyclic nitrogen atoms while the Ad and Gu exocyclic NH_2 groups and the GuCO group are not involved in the coordination.

The NMR spectra of the solutions of the complexes obtained and their deuterated derivatives in DMSO-d_6 have permitted us to suggest that Ad in these complexes acts as a bridge ligand: two Pt(II) atoms add simultaneously to two Ad molecules. All Ad heterocyclic atoms seem to contribute to the formation of the bond with Pt(II) to give a mixture of coordination isomers which gives a complicated picture of the NMR spectra of (I). In (II) Gu acts as a monodentate ligand that interacts with a Pt^+ ion in a keto-form. The Pt(II) atom adds to Gu *via* N7. The GuCO group with a H_2O coordinated molecule forms an intramolecular hydrogen bond.

Biological tests with animals indicate that (I) has moderate antitumour activity, while (II) displays well-defined anti-cancer properties. Both complexes are practically non-toxic.

T10

Hydroxoaquo(3,3′,3″-triaminotripropylamine)cobalt-(III) Ion. A Highly Effective Reagent for Promoting the Hydrolysis of Phosphate Species

GULNAR RAWJI, MARKUS HEDIGER and RONALD M. MILBURN

Department of Chemistry, Boston University, Boston, Mass. 02215, U.S.A.

In earlier work we demonstrated the effectiveness of tn_2Co^{III}(aq) in promoting the hydrolysis of phosphate esters [1] and polyphosphates [2–4] [tn = $H_2N(CH_2)_3NH_2$; (aq) = $(OH_2)_2$, (OH)(OH_2) or $(OH)_2$ depending on pH; charges omitted]. Such studies can provide insight into possible roles for metal centers in biological phosphoryl transfer. Under appropriate conditions tn_2Co^{III}(aq) produces, on direct addition to phosphate species, accelerations in hydrolysis of up to $\sim 10^5$.

Using the tripodal ligand trpn [=$N(CH_2CH_2CH_2NH_2)_3$] we have now prepared $trpnCo^{III}$(aq); this reagent is significantly more effective than tn_2Co^{III}(aq) in promoting hydrolysis of phosphate esters and polyphosphates. Here we compare the reactivities of $trpnCo^{III}$(aq) and tn_2Co^{III}(aq) towards adenosine 5′-diphosphate (ADP), bis(2,4-dinitrophenyl) phosphate [$(2,4\text{-DNP})_2P$], and 2,4-dinitrophenyl phosphate [2,4-DNPP] [5].

For hydrolysis studies on ADP (20 °C) the N_4Co^{III}ADP 1:1 complex was pre-formed at pH 4.0 prior to addition of further N_4Co^{III}(aq) and pH adjustment to 7.0; reaction was followed by ^{31}P NMR analysis of solutions quenched with NaOH [3, 4]. Hydrolysis studies on $(2,4\text{-DNP})_2P$ and 2,4-DNPP were at 25 °C ($\mu = 0.50$ *M*) with direct mixing of ester and N_4Co^{III}(aq) solutions; reaction was followed spectrophotometrically from production of 2,4-dinitrophenolate.

Table I compares rates for hydrolysis of ADP to AMP and P_i for the two cobalt reagents. In both cases the 1:1 complex is formed almost quantitatively and is of low reactivity, while excess N_4Co^{III}(aq) leads to marked increases in rate. The most noticeable new feature is the much higher reactivity observed for $trpnCo^{III}$(aq) compared to tn_2Co^{III}(aq). At the highest ratio studied (8:1) the half-life for the trpn system is <1 min, which corresponds to an acceleration over the unpromoted reaction of $>1 \times 10^6$ [7].

TABLE I. ADP Hydrolysis Promoted by N_4Co^{III}(aq)[a].

Co/ADP	$k \times 10^4$ (sec^{-1})		k_{trpn}/k_{tn_2}
	$trpnCo^{III}$(aq)	tn_2Co^{III}(aq)[b]	
1:1	≤0.2	0.2	≤1
2:1	8.2	2.3	3.6
4:1	42.0	7.3	5.8
8:1	>150.0	13.4	>10.0

[a]ADP = 0.020 *M*, 20.0 °C, pH 7.0. 1:1 complex pre-formed at pH 4.0 and 20 °C for 60 min at a concentration 0.3 *M* for both reactants. [b]Results from ref. 4.

Figure 1 summarizes results for the hydrolysis of 2,4-DNPP and $(2,4\text{-DNP})_2P$ in the presence of $trpnCo^{III}$(aq). At the pH corresponding to maximum rates [which approximates the pH at which trpnCo(OH)$(OH_2)^{2+}$ is maximized in solutions of $trpnCo^{III}$(aq)] the diester reacts 25 times faster than in the presence of tn_2Co^{III}(aq) at its pH maximum (otherwise comparable conditions); a similar comparison for the monoester favors trpn over tn_2 by a factor of 30 [8].