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The Interaction of Transition Metal Ions with 8-Azapurines

NIKOS KATSAROS* and ANDRIANA GRIGORATOS

Chemistry Department, Nuclear Research Center 'Demokritos', Aghia Paraskevi, Athens, Greece

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Abstract

Cu(II), Pd(II), Au(III) with 8-azaguanine, Co(II), Au(III) and Au(I) with 8-azahypoxanthine and Zn(II), and Pt(II) with 8-azaadenine complexes were isolated from aqueous or methanolic solutions at appropriate pH. The new complexes which are insoluble in organic media were characterized by elemental, infrared, diffuse electronic spectral and magnetic measurements. Probable structural types involve polymeric structures where the azapurines behave as bidentate bridging ligands. Such structures are discussed in relation to the nitrogen atoms involved in coordination.

Introduction

The interaction of transition metal ions with nucleic acid bases, nucleosides and nucleotides has been the subject of numerous recent chemical, spectroscopic and crystallographic studies [1–9] due to the biological significance of metal–nucleic acid interactions and the discovery that some of these complexes are potential chemotherapeutic agents [10–12].

Crystallographic studies have demonstrated that various transition metal ions can bind in many different ways to a given purine or pyrimidine base. For example, Zn(II) binds to N(7) in adenine [13], Cu(II) binds to N(9) [14], and Zn(II) binds to N(9) in guanine [15]. Thus, the various transition metal ions would be expected to produce different effects on the hydrogen bonding scheme in a polynucleotide chain; this may partially explain the observation that some metal ions (e.g. Cu^{2+}, Cd^{2+}, Hg^{2+}, Rh^{3+}) lower the thermal denaturation temperature of DNA, while others (e.g. Zn^{2+}, Mn^{2+}, Mg^{2+}, Rh^{3+}) have the reverse effect [16–18].

The synthesis and structure of aza-analogs of the nucleic acid constituents have been extensively studied during the past decade [19–30], mainly because of the demonstrated but varying potency of some of these species (notably 8-azaguanine) as antitumor agents [29–35]. On the basis of structural models, it has been suggested that the biological activity of the ortho azanucleosides (*i.e.* 6-aza pyrimidene or 8-azapurine nucleosides) may result in changes in their hydrogen bonding ability brought about by conformational changes [36]. This postulate received partial confirmation from theoretical [37] and crystallographic studies, which have shown that the conformations of azanucleosides about the glycosyl bond are in different angular ranges than are those of the naturally occurring nucleosides [25, 26, 28, 29]. Metal coordination of the ortho azanucleosides may further change the electronic properties of the base and hence the hydrogen base-pair interactions in the polynucleotide.

Very few studies concerning the interaction of 8-azapurines and 6-azapyrimidines with metal ions have been reported in the literature. The first reported interaction in the series was that of 8-azaadenine with Cu(II); in that reaction, however, ring-opening of the base at the C(2) position occured to form tetrachlorobis-2-(5-amino-4-carboxamidinium){1,2,3}triazole-copper(II) [38]. In the other two structurally known complexes with 8-azapurines, trichloro(8-azaadeninium)zinc(II) and bis(8-azahypoxanthinato)-tetraaquo cadmium(II), the metal ion is coordinated through the N(3) in the former [39] and to the N(7) in the later [40]. In the only structurally known complex with 6-azapyrimidine, that of Cu(II) with 6-azauracil, the metal ion interacts with the ligand through the N(3) [41]. Finally, potentiometric studies in aqueous solutions of 8-azaadenine and 8-azaguanine with various transition metal ions have been published [42–44]. These are to our knowledge, the only reports in the literature concerning complexes with this type of ligand.

The goal of the present study was to synthesize and characterize by physical and chemical methods a series of stable complexes of transition metal ions with 8-azapurines in order to investigate the nature of the interactions in these systems.

Experimental

Materials

All the chemicals were reagent grade and used without any further purification. The aza compounds

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*Author to whom correspondence should be addressed.

were purchased from Sigma Chem. Co., and the metal halides were from Fluka A.G. DMSO was purified by vacuum distillation after drying over calcium hydride.

Microanalyses

Carbon, hydrogen, nitrogen analyses were performed by the analytical group of N.R.C. 'Demokritos'. Chlorine was determined colorimetrically by the method of Loog *et al.* [45].

Magnetic Measurements

Magnetic susceptibilities were measured at room temperature by the Faraday method using a Cahn R.G. Electrobalance PAR Model 155 with $HgCo(NCS)_4$ as a standard.

Conductivity Measurements

The measurements were carried out in DMSO at 25 °C by means of an E365B conductoscope, Metrohm Ltd., Herisau, Switzerland. Λ_m values are expressed in $ohm^{-1}\ cm^2\ mol^{-1}$.

Infrared Spectra

The infrared spectra (4000–200 cm^{-1}) in potassium bromide discs were recorded with a Perkin-Elmer Model 521 Grating Spectrophotometer.

Diffuse Electronic Spectra

Diffuse reflectance spectra were recorded on a Varian 634 Model at room temperature.

Preparations

$Zn(8\text{-aa})_2Cl_2 \cdot H_2O$ was prepared by gradually adding and stirring an acidic solution of $ZnCl_2$ (1 mmol of $ZnCl_2$ in 4 ml of 0.36 M HCl) into a solution of 8-azaadenine (1 mmol of 8-azaadenine in 40 ml of 0.36 M HCl). On standing, under refrigeration a white microcrystalline compound, precipitated, which was filtered off, washed with water and alcohol and dried in vacuum over P_2O_5.

$Pt(8\text{-aa})Cl_2$ was prepared gradually adding and stirring a solution of K_2PtCl_4 (0.025 mol of K_2PtCl_4 in 5 ml of H_2O) into a suspension of 2 mmol of 8-azaadenine in 15 ml of H_2O. The mixture was stirred for 3 days; by that time the color of the mixture changed to yellow, indicating that a reaction took place. The precipitate was filtered, washed with water and alcohol and dried in vacuum over P_2O_5.

$Cu(8\text{-ag})(OH)_2 \cdot 5H_2O$ was prepared by adding a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol of $Cu(NO_3)_2$ dissolved in 5 ml of H_2O) gradually under stirring to a basic solution of 8-azaguanine (1 mmol of 8-azaguanine to 30 ml of 0.1 N NaOH). The solution turned green and on standing a green precipitate was formed. Upon filtration, the precipitate was washed with alcohol and dried *in vacuo* over P_2O_5.

$Pd(8\text{-ag})Cl_2$ was prepared with a similar procedure to that described above for the $Cu(8\text{-ag})(OH)_2 \cdot 5H_2O$; a yellow powder was formed.

$Au(8\text{-ag})Cl_3$ was prepared by dissolving 1 mmol of $HAuCl_4 \cdot xH_2O$ in 5 ml of H_2O, neutralizing the resulting solution with concentrated sodium hydroxide, and adding to it a basic solution of 8-azaguanine (1 mmol of 8-azaguanine in 30 ml of 0.1 N NaOH). Upon mixing, the resulting solution turned red–brown; it was heated to 35 °C until it was reduced to one-half of its volume, and upon refrigeration, gave a red–brown precipitate. The precipitate was filtered, washed repeatedly with water and alcohol and dried in vacuum over P_2O_5.

$Co(8\text{-ahx})_2Cl_2$ was prepared in a procedure similar to that described for $Au(8\text{-ahx})Cl_3$; an orange product was isolated.

$Au(8\text{-ahx})Cl \cdot H_2O$ was prepared by adding 0.339 g of $HAuCl_4 \cdot xH_2O$ to a one molar oxygen-free water solution of vitamin C. Au(III) was reduced to Au(I). To this solution an aqueous solution of 8-azahypoxanthine (0.164 g of 8-azahypoxanthine dissolved in 25 ml of H_2O) was added gradually under stirring. On standing a yellow–orange precipitate was formed, which was filtered, washed repeatedly with water, and dried in vacuum over P_2O_5.

Results and Discussion

The elemental analyses and other physical properties of the prepared compounds are listed in Table I. The complexes were not very soluble in water or DMSO. However, the solubilities in these solvents allowed for some conductivity measurements. The equivalent conductance values at 1×10^{-3} molar concentrations indicated that Zn^{2+}, Pt^{2+} complexes with 8-azaadenine and Au^{3+} complex with 8-azaguanine are 1:1 electrolytes in DMSO. The low values observed are probably due to the bulkiness of the cations and possible ion-pair formation. The conductivity measurements were taken immediately after preparation of the solutions since it was observed that conductivity values increase with time, indicating that the solvent is reacting with the complexes.

Infrared Spectra

The infrared spectra of the complexes are given in Table II. In the region 4000–3000 cm^{-1} several strong broad bands appeared, attributed to $-NH_2$ and $-OH$ stretching modes, overtone and combination bands, and intramolecular hydrogen bonding [46–48]. Purines exhibit four possible coordination sites of the purine ring, N(1), N(3), N(7) and N(9), in addition to the characteristic group(s). Among these, the preferred binding sites are N(7), N(9), with N(1) and N(3) being less favorable [7–9]. In addition, crystallographic evidence from a large number of

TABLE I. Analytical Data for the Complexes.

Complex	Color	Analysis [Found (Calc.)]%				Decomposition temperature (°C)	μ_{eff} (B.M.)	Λ ($cm^2 \times ohm^{-1} \times mol^{-1}$)
		C	H	N	Cl			
$Zn(8\text{-}aa)_2Cl_2H_2O$	white	22.11	2.21	39.49	16.59	205	D	
		(22.50)	(2.24)	(39.38)	(16.63)			
$Pt(8\text{-}aa)Cl_2$	yellow	12.02	0.99	20.24	17.69	270	D	20.95(31.50) (DMSO)
		(11.93)	(0.99)	(20.09)	(17.64)			
$Cu(8\text{-}ag)(OH)_2 \cdot 5(H_2O)$	green	12.18	4.92	22.34	21.03	285	0.98	18.24(25.36) (DMSO)
		(12.74)	(4.86)	(22.30)	(20.87)			
$Pd(8\text{-}ag)Cl_2$	yellow	14.37	1.24	25.97	21.45	310	D	9.99(14.80) (DMSO)
		(14.57)	(1.21)	(25.50)	(21.52)			
$Au(8\text{-}ag)Cl_3$	red-brown	11.50	0.94	18.36	23.61	192	D	
		(11.53)	(0.95)	(18.44)	(23.35)			
$Co(8\text{-}ahx)_2Cl_2$	orange	23.56	1.39	33.76	17.69	210	4.73	32.72(52.42)(H_2O)
		(23.76)	(1.49)	(34.65)	(17.55)			
$Au(8\text{-}ahx)Cl_3$	orange	10.45	0.65	15.86	24.39	205	D	36.55(60.94) (DMSO)
		(10.90)	(0.68)	(15.89)	(24.15)			
$Au(8\text{-}ahx)ClH_2O$	brown	11.92	1.31	15.83	9.42	245	D	
		(11.38)	(1.29)	(15.48)	(9.15)			

TABLE II. Infrared Data for the 8-Azapurine Complexes (cm^{-1}).

Assignment	8-aa	Zn(II)–(8-aa)	Pt(II)–(8-aa)
ν_{asNH_2}	3260(s, br)	3560(s, br)	3500(s, br)
ν_{OH}	3120(s, br)	3340(s, br)	3300(s, br)
ν_{sNH_2}	2925(s, br)	3180(s, br)	3050(s, br)
δ_{NH_2}	1710(s)	1680(s, br)	1670(s, br)
$\nu_{pyr.\ ring}$	1620(s)	1610(s, br)	1630(s)
ν_{NNN}	1610(s)	1600(s)	1600(s, br)
$\nu_{pyr.\ ring}$	1440(s)	1440(m)	1430(m)
ν_{NNN}	1375(m)	1385(m)	1380(m)
ν_{NNN}	1340(s)	1360(s)	1345(m)
ν_{NN}	1320(s)	1300(m)	1320(m)
ν_{sNNN}	1220(s)	1220(s)	1220(m)
$\nu_{\alpha sNH_2}$	1170(m)	1180(m)	1180(w)
	1065(m)	1070(m)	1060(w)
	1090(m)	1040(m)	1050(m, br)
ν_{NH_2}	1000(s)	1020(m)	1020(w)
	980(m)	990(m)	980(w)
	930(s)	930(m)	920(m)
γ_{CH}	800(m)	800(w)	780(w)
$\gamma_{\alpha sNH_2}$	720(s)	720(w)	720(w)

Assignment	8-ahx	Co(II)–(8-ahx)	Au(III)–(8-ahx)	Au(I)–(8-ahx)
ν_{asNH}	3500(s, br)	3380(s, br)	3100(s, br)	3260(s, br)
ν_{OH}	3320(s, br)	3300(s, br)	3050(s, br)	3100(s, br)
ν_{sNH}	3220(s, br)	3200(s, br)	2980(s, br)	3040(s, br)
$\nu_{C=O}$	1730(s)	1690(s)	1690(s)	1705(s, sh)
δ_{NH_2}, $\nu_{pyr.\ ring}$	1680(s)	1670(s, br)	1670(m, sh)	1680(s)

(Continued)

TABLE II. *(Continued)*

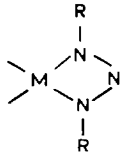
ν_{NNN}	1600(s)	1600(s)	1580(s)	1580(s)
δ_{NH}	1525(m)	1530(m)	1510(m)	1520(w)
γ_{NNN}	1380(m, shp)	1380(s, shp)	1380(m, shp)	1380(w, shp)
ν_{NH}	1370(m, shp)			
γ_{sNN}	1270(s)	1275(m, shp)	1270(m, shp)	1260(s)
ν_{NN}	1230(w)	1200(m)	1230(m)	1230(s)
$\nu_{\alpha sNH_2}$	1160(m)	1160(w)	1160(m)	1155(m)
	1010(m)	1010(m)	1000(m, shp)	1000(w)
ν_{C-N}	1100(m)	1110(m)	1100(m)	1090(w)
ν_{CH}	790(s)	790(s, br)	780(s, shp)	790(m, shp)
$\gamma_{\alpha sNH_2}$	720(m)	720(w, shp)	720(w, sh)	730(w, sh)

Assignment	8-ag	Cu(II)–(8-ag)	Pd(II)–(8-ag)	Au(III)–(8-ag)
ν_{asNH_2}	3340(s, br)		3420(s, br)	
ν_{OH}	3270(s, br)	3400(s, br)	3320(s, br)	3300(s, br)
ν_{sNH_2}	3160(s, br)		3200(s, br)	
$\nu_{C=O}$	1710(s)	1690(m)	1700(s, br)	1700(m)
δ_{NH_2}	1670(s)	1655(s, sh)	1655(s)	1670(s, sh)
$\nu_{C=N}$, $\nu_{C=O}$	1625(m)	1620(s, sh)	1610(s)	1620(s)
ν_{NNN}	1600(s)	1600(s)	1600(s)	1600(s)
ν_{C-N}, $\nu_{C=O}$	1550(m)	1545(m)	1560(s)	1550(s, br)
$\nu_{pyr.\ ring}$	1400(m)	1390(s)	1400(m, sh)	1400(m)
ν_{NNN}	1360(m)	1365(m, sh)	1370(w, br)	1355(m)
ν_{NN}	1260(s, shp)	1260(w)	1280(m)	1270(m)
ν_{NNN}	1170(s, shp)	1190(w)	1170(s)	1170(m)
	990(m)	1020(w)	1020(w)	1020(w)
ρ_{NH_2}	850(s, shp)	840(w)	850(w)	850(w)
γ_{CH}	790(m, shp)	800(w, shp)	785(m)	780(w)
$\gamma_{\alpha sNH_2}$	700(m, shp)	690(m)	680(w, br)	680(w)

complexes with adenine, guanine and their nucleosides and nucleotides, suggests that the amino group does not participate in coordination [7–9]. However, in a number of complexes with guanine, guanosine, hypoxanthine and xanthosine, the metal ion interacts with the carbonyl oxygen [7–9].

Azapurines have, in addition to N(1), N(3), N(7), N(9), also the N(8) position as a potential coordination site. Of the five possible coordination sites of the purine ring, three of them, N(7), N(8) and N(9) of the triazole group, exhibit considerable basicity; the N(3) position is more basic than in the respective nucleic acid bases [49].

Before discussing the structure and properties of individual complexes, we review the general approach used to arrive at the structural assignments of the complexes, and, in particular, whether the ligand behaves as a monodentate binding to the metal through one of the three nitrogens of the triazole group, or as a bidentate bridging ligand. Structures involving monodentate, chelate and bridging 1,3-diaryltriazenido ligands have previously been postulated, and criteria based on infrared spectroscopy have been reported distinguishing between these three modes of bonding [50, 51].

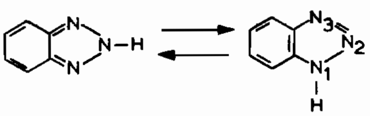


I

Class A complexes (using nomenclature adopted by Knoth) gave spectra containing bands at 1260–1300 cm^{-1} and 1580–1600 cm^{-1} attributable to the triazenido group, and were formulated as chelate trazenido complexes (I). Class B compounds showed bands at 1150, 1190–1210, 1260–1300 and 1580–1600 cm^{-1}, which were attributed to the presence of monodentate 1,3-diaryltriazenido ligands. Bridging 1,3-diaryltriazenido ligands also gave infrared spectra typical of class B compounds. The absorptions that distinguish the two classes are those at 1150 and 1190–1210 cm^{-1}. The 1150 cm^{-1} absorption band is not very intense, and in some cases the assignment of this band was not easy. The 1190–1210 cm^{-1} absorption was the most reliable criterion for assignment of the complexes to class A or class B. These empirical infrared criteria permitted rational and self-consistent asssignments of structure to be made for more than sixty compounds with this and related types of ligands [50–52]; several of them have since been verified by X-ray crystallographic analysis [53–56].

An attempt was made to differentiate between monodentate and bidentate bridging structures in some triazenido complexes [63, 64]. It was observed that, in addition to the vibrations attributable to class B complexes, a bridging triazenido group has a characteristic azenido skeletal vibration in the range 1350–1375 cm^{-1} (class C). More information is necessary to assess the accuracy of this suggestion.

A large number of complexes have been prepared with benzotriazole, protonated (BTAH) or deprotonated (BTA^-), and related ligands [57]. Benzotriazole is a versatile ligand, existing in two possible tautomeric forms (**II**). The most common mode of bonding for neutral monodentate benzotriazole to metal ions seems to involve N(3) in BTAH. This structure has been verified by X-ray crystallographic analysis for $\text{Zn(BTAH)}_2\text{Cl}_2$ [58], and has been suggested for a number of similar complexes investigated by spectroscopic techniques [57].



II

In the case of bidentate binding, it was not clear whether the –N(2) or N(1)–N(3) pair is involved. In a large number of complexes with protonated or deprotonated benzotriazole, bidentate through N(1)–N(3) or N(1)–N(2) or tridentate bridging structures have been proposed on the basis of infrared spectroscopy [57] and X-ray crystallographic analysis [59–62].

We have applied the spectroscopic criteria reported for class B complexes with triazenido and related ligands to complexes with protonated benzotriazole. The application of these criteria verified the proposed structures for benzotriazole complexes and suggested that in the complexes prepared with 8-azaadenine, 8-azaguanine and 8-azahypoxanthine, the ligands behave as monodentate or more likely, considering the high insolubility of the complexes and the spectroscopic criteria suggested by Vrieze *et al.* [63, 64], as bidentate bridging entities.

The tentative assignments of 8-azaadenine were based on the vibrational modes of adenine and the –N=N–N– vibrations of diaryltriazene and benzotriazole [52, 57]. The vibrations assigned to the triazolo group in 8-azadenine are at 1605, 1320, 1220 and 1170 cm^{-1}. In the complexes of 8-azaadenine with Zn(II) and Pt(II), the absorptions at 1180 and 1120 cm^{-1} strongly suggest that these complexes exhibit monodentate or polymeric bridging structures.

TABLE III. Pertinent Infrared Data for the 8-Azapurine Complexes (cm^{-1}).

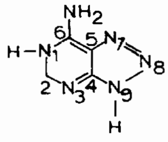
(8-ag)	Cu(II)–(8-ag)	Pd(II)–(8-ag)	Au(III)–(8-ag)	(8-ahx)	Co(II)–(8-ahx)	Au(III)–(8-ahx)	Au(I)–(8-ahx)	Assignment
1710s	1690m	1700s, br	1700m	1730s	1690s	1690s	1705s	C=O
1680s	1650s	1645s	1680s	1680s	1660s		1690s	δ_{NH_2}
1600s	1600s	1600s	1600s	1600s	1600s	1580s	1570s	NNN
1280s	1260w	1280m	1260m	1270s	1275m	1270s	1260s	NN
1170s	1190w	1150s	1160m	1160w	1160w	1160w	1150m	NN

8-aa	Zn(II)–(8-aa)	Pt(II)–8-aa)	Assignment
1620s	1610s	1610s	ν_{ring}
1605s	1600s		NNN
1320s	1310m	1320s	NN
1170s	1180m	1180w	NN

Vrieze *et al.* assigned an additional band observed in the range 1350–1390 cm^{-1} in a number of triazenido complexes to bridging triazenido group (Class C) [63, 64]. In all of the complexes prepared, the presence of bands in the region 1340–1400 cm^{-1} cannot be assigned with certainty since the pure ligands also exhibit absorptions in that area. However, taking into consideration the presence of these bands and the high insolubility of the complexes, bridging structures are favored.

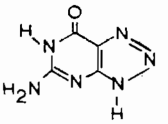
Numerous crystal structure determinations of metal complexes with protonated, deprotonated or neutral adenine have established that, when it is functioning as a terminal unidentate, the ligand usually coordinates through N(9) [7–9]. The only reported exception is Zn(adeninium)Cl_3, in which the cationic ligand coordinates through N(7) to the metal [13]. When acting as bridging bidentate, adenine has been found to coordinate through N(3), N(9) in Cu^{2+} complexes [66–68] and through N(7), N(9) in CH_3Hg^+ complexes [69]. The recent work of Beauchamp and Hubert on CH_3Hg^+ [70] complexes with adenine and 9-methyl adenine has demonstrated that any of the four nitrogens of adenine (*i.e.* N(1), N(3), N(7), N(9)) can function as a binding site, provided that steric effects do not hinder its coordination to the metal ion [71]. From the above discussion, it is evident that the most likely binding site for adenine complexes is N(9) for monodentate bridging ligands.

There are no crystallographic data concerning the site of protonation in the triazole portion of free neutral 8-azaadenine. The crystal structure of 8-aza adenine hydrochloride (**III**) indicates that the N(1) atom is protonated [72]. Unfortunately the triazole proton could not be located. However, in a copper complex [38] with a triazole derivative and a zinc complex with the 8-azadeninium cation, it was suggested that the triazole proton is located on N(8) [39]. In the complex trichloro (8aaH)zinc(II) [39], the metal ion is binding to the ligand at N(3), while in the copper complex $\{CuCl_4(HACT)_2\}'$ (where HACT = 5-amino-4-carboxamidinium-1,2,3,triazole), metal coordination occurs at N(8) and protonation at N(9). However Pullman and Pullman [75] have calculated that the preferred site for the proton is N(7). Although bidentate bridging most probably occurs through N(3)–N(9) or N(7)–N(9), the possibility of any pair of nitrogens participating in the polymeric bridging cannot be excluded [79–83].

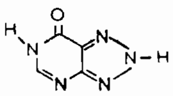


III

In the complexes with 8-azaguanine and 8-azahypoxanthine, in addition to the nitrogens of the five member ring, the carbonyl oxygen is also a potential binding site. In the infrared spectra of 8-azaguanine and 8-azahypoxanthine, the C=O absorption band appeared at 1710 and 1730 cm^{-1} respectively. In a large number of complexes where the metal ion coordinates through the oxygen of the carbonyl group, a decrease in the C=O stretching mode occurs [65]. This decrease in frequency is usually more than 70 cm^{-1}. In the complexes prepared, the carbonyl absorption band is shifted to lower wave numbers by 10–20 cm^{-1}, suggesting that the metal ion does not bind through the carbonyl oxygen. The small shift observed may be an indication that the metal ion coordinates through the nitrogen(s) of the triazole group. The absorption bands at 1600, 1280 and 1170 cm^{-1} are assigned to the N–N=N group vibrational modes. In the complexes of 8-azaguanine with Au(III), Pd(II) and Cu(II), the absorption bands of the triazole group appeared at 1600, 1260 and 1190 cm^{-1}. The positions and the shapes of these bands strongly suggest that 8-azaguanine behaves as a monodentate or bidentate bridging ligand. In addition, the presence of a band around 1370 cm^{-1}, along with the high insolubility of these complexes, favors bridging structures [63, 64].



IV



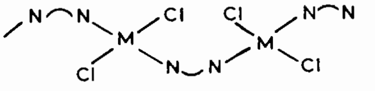
V

The crystal structure of 8-azaguanine monohydrate (**IV**) proved that N(1) and N(9) positions are protonated and that N(3) is more basic than N(7) [76]. Thus bidentate bridging can take place through any two of the N(3), N(7), N(8) nitrogens.

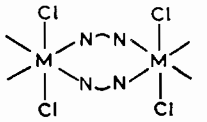
The stretching modes of the triazolo group in 8-azahypoxanthine appeared at 1600, 1270, 1230 and 1160 cm^{-1}. In the complexes of 8-azahypoxanthine with Co(II), Au(III) and Au(I), the absorptions at 1600–1570, 1275–1260, 1230–1200 and 1160 cm^{-1} are attributed to N–N=N vibrational modes along with a sharp band around 1370 cm^{-1} [63, 64]; this suggests that these complexes also exhibit polymeric bridging structures. The crystal structure of 8-azahypoxanthine (**V**) indicates that N(1) and N(8) positions are protonated; the most basic site is N(9) [77]. The crystal structure of bis (8-azahypoxanthinato)tetraaquocadmium(II) [40] shows that the geometry around cadmium(II) is roughly octahedral with the hypoxanthinato ligands coordinated through N(7), indicating that with soft metals the N(7) position is also a possible coordination site. Thus, in the present complexes with 8-azahypoxanthine, any two of the three nitrogens N(3), N(7), N(9) can participate in polymeric bridging.

In all of the complexes prepared with 8-azapurines, the C=N(3) stretching vibrations of the pyrimidene ring appeared in the same position as that of the free ligands, indicating that N(3) probably does not participate in coordination. However, this possibility cannot be excluded with certainty since, for a large number of complexes, the purine ligand coordinates to the metal through N(1) or N(7). They do not exhibit drastic changes in their infrared spectra. Furthermore there are no infrared data for complexes of related ligands where the metal ion coordinates through N(3).

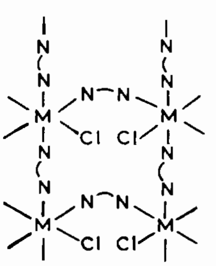
The platinum(II) and palladium(II) complexes with 8-azaadenine and 8-azaguanine must involve bridging bidentate ligands (designated as N N) in order to be tetracoordinated, or of square planar geometry. Probably these compounds have a single bridged linear chainlike polymeric structure (type (**VI**)) similar to those previously postulated for many 3d metal complexes with purine and adenine [73].



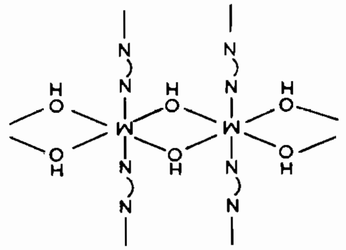
VI



VII



VIII



IX

In the case of zinc(II) and cobalt(II) complexes with 8-azaadenine and 8-azahypoxanthine, both of the purinic ligands would be bidentate in order to be hexacoordinated. The double-bridge linear polymeric structure (**VII**) is the simplest, but a more complicated cross-linked structural type such as (**VIII**), which involves cross linkage between single-bridged–M–L–M–L– sequences, may be more compatible with the normal room temperature - magnetic moments of the Co^{2+} complexes. The very low magnetic moment of the Cu^{2+} complex [74] with the 8-azaguanine ligand indicates that a cross-linked polymeric structural formula such as (**IX**) exists, which involves double-bridged linear polymeric structures through hydroxyl group cross-linked between –M–L–M–L– sequences. Finally, for the gold(III) and gold(I) complexes with 8-azaguanine and 8-azahypoxanthine, 1:1 ionic single-bridged linear polymeric structures are proposed to satisfy the square planar and linear geometry, respectively.

Electronic Spectra

The diffuse electronic spectra of the complexes in the solid state are given in Table IV. Only one absorption is observed for each of the complexes Pt(8-aa)-Cl_2 and Pd(8-ag)Cl_2, at 650 and 640 nm, respectively. These bands are attributed to d–d transitions ($^1B_{1g}$ $^1A_{1g}$). The rest of the absorption bands cannot be observed, as happens with a number of platinum(II) and palladium(II) complexes [75].

TABLE IV. Spectroscopic Properties of the Complexes.

Complex	λ(nm)	Assignment	
Pt(II)–(8-aa)	650	$^1B_{1g}$	$^1A_{1g}$ (d–d)
Pd(II)–(8-ag)	640	$^1B_{1g}$	$^1A_{1g}$ (d–d)
Au(III)–(8-ag)	490	$^1A_{2u}$	$^1A_{1g}$ (L M, C.T.)[a]
Au(III)–(8-ahx)	465	$^1A_{2u}$	$^1A_{1g}$ (L M, C.T.)[a]
Cu(II)–(8-ag)	845	(d–d)	
	640	(d–d)	
	410	(M L, C.T.)[a]	
Co(II)–(8-ahx)	1051	$^4T_{2g}$	$^4T_{1g}$ (F)
	501	$^4A_{2g}$	$^4T_{1g}$ (F)
	462	$^4T_{1g}$(P)	$^4T_{1g}$ (F)

[a] Charge transfer transition from metal to ligand or the opposite.

The energy difference Δ_1 between 4 a_g and 3 b_{1g} orbitals is calculated from the formula:

$$\Delta_1 = V_1 + 3.5F_2 \ (F_2 = 600 \text{ cm}^{-1})$$
$$\Delta_1 = 15\,385 + 2100 = 17\,485 \text{ cm}^{-1} \text{ for Pt(II)}$$
$$\Delta_1 = 15\,625 + 2100 = 17\,725 \text{ cm}^{-1} \text{ for Pt(II)}$$

The diffuse electronic spectra and the Δ_1 values for Pt(II) and Pd(II) complexes are characteristic of square planar geometry [76]. The positions and the number of electronic absorptions of the complex Cu(8-ag)$(OH)_2 \cdot 5H_2O$ suggest octahedral symmetry with tetragonal distortion [77]. Similarly the electronic spectrum of Co(8-ahx)Cl_2 indicates octahedral geometry. The 10 *Dq* and the Racah electronic parameter *B* are calculated from the formula [78]:

$$340Dq^2 + 18(V_3 - 2V_3)Dq + V_2^2 - V_2V_3 = 0$$

$$B = \frac{V_3 - 2V_2 + 3Dq}{15}$$

From the Racah parameter for the free ion $Bf = 967$ we calculate the parameter $B = B_{complex}/Bf = 1.30$.

The value of the parameter *B* indicates weak covalent bonding between the metal ion and the ligand. Finally, charge transfer bands occur in the complexes of Au(III) and Au(I) with 8-azahypoxanthine and 8-azaguanine.

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