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Gold(III) and Platinum(II) Complexes of Hexamethylenetetramine

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Gold(III) trichloride and platinum(II) dichloride form 1:1 complexes with hexamethylenetetramine. The compounds prepared were characterized by the elemental analysis, infrared, *Raman*, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, and conductivity measurements.

[Keywords: Gold(III)trichloride; Hexamethylenetetramine; Infrared; NMR spectroscopy; Platinum(II) dichloride]

Gold(III)- und Platin(II)-Komplexe mit Hexamethylentetramin

Gold(III)trichlorid und Platin(II)dichlorid bilden mit Hexamethylentetramin 1:1-Komplexe. Die isolierten Verbindungen wurden mittels Elementaranalyse, IR, *Raman*, ^{1}H- und ^{13}C-NMR und Leitfähigkeitsmessungen charakterisiert.

Introduction

It has been known that hexamethylenetetramine (*hmta* = 1, 3, 5, 7 tetraazatricyclo[3.3.1.1]decane) forms a number of complexes with transition metal ions[1–3]. With some hydrated metal salts hexamethylenetetramine forms molecular complexes of the type $M(ClO_4)_2 \cdot 8\,H_2O \cdot 2\,hmta$ (M = Mg, Ca, Sr, Ba, Zn, Cd, Co and Ni) (Ref.[10]). *Kovacs* et al. found by X-ray analysis that the crystals of $Mg(hmta)_2Cl_2 \cdot 10\,H_2O$ and $Ca(hmta)_2Br_2 \cdot 10\,H_2O$ belong to the triclinic system and these complexes are formulated as $[M(H_2O)_6X_2] \cdot 2\,hmta \cdot 4\,H_2O$ (Ref.[4,5]), while the complexes $CoX_2(hmta) \cdot 6\,H_2O$ and $NiX_2(hmta) \cdot 6\,H_2O$ are formulated as $[M(H_2O)_4X_2] \cdot (hmta) \cdot 2\,H_2O$ (Ref.[1]). *Buhannic* and *Guerchais*[6] assigned

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the infrared bands of the complexes $MX_2(hmta)$ and $MX_2(hmta)_2$ [M = Co(II), Zn(II), X = halide pseudohalide ions] to various vibrational modes of *hmta* indicating that the T_d symmetry of free *hmta* is lowered to C_{3v} symmetry in $MX_2(hmta)_2$ and C_{2v} in $MX_2(hmta)$. Hexamethylenetetramine is potentially a tetradentate ligand; stereochemically, it is more likely to act as a bridging group rather than a chelate. In a number of complexes of transition metal ions with hexamethylenetetramine spectroscopic studies indicated that the metal ion is interacting directly with a nitrogen of the ligand[7–10]. In the complexes with Cu(II), Cd(II), Hg(II), and Ag(I) these results have been verified recently by X-ray crystallography[11–13].

Gold complexes of nitrogen donors play an important role in modern chrysotherapy[14,15] and platinum complexes of nitrogen donors are also of biological interest because of their antitumor and antibacterial activity[16,17]. This work describes an investigation into the preparation of gold trichloride and platinum dichloride complexes of hexamethylenetetramine. Their infrared spectra are examined and structural implications considered by comparison with the spectra of related complexes whose crystal structures have been determined recently.

Experimental

Hexamethylenetetramine (Merck), $HAuCl_4 \cdot xH_2O$ (Riedel-deHaen AG) K_2PtCl_4 (Fluka AG) were reagent grade and used without further purification. The complexes were prepared by mixing equimolar aqueous solutions of the corresponding metal salts with the hexamethylenetetramine solution. From this mixture the complexes were precipitated immediately, washed with alcohol, ether, and dried under high vacuum. The gold complex was also prepared by mixing equimolar aqueous or methanolic solutions of $HAuCl_4 \cdot xH_2O$ with the respective hexamethylenetetramine solution.

Infrared spectra (4 000-200 cm^{-1}) in potassium bromide discs were recorded with a Perkin-Elmer Model 521 Grating Spectrophotometer. The ^1H and ^{13}C NMR spectra were measured in d_6-*DMSO* using an XL-100-15 NMR spectrometer. The chemical shifts are related to *TMS* as internal standard at ambient temperatures. Conductivity measurements were carried out in *DMSO* at 25 °C by means of an E 365 B conductoscope, Metrohm Ltd., Herisau, Switzerland.

Results and Discussion

The complexes prepared, their elemental analysis and other physical properties are listed in Table 1. $PtCl_2(hmta) \cdot 2\,H_2O$ was insoluble in water and all other common organic solvents; $AuCl_3(hmta)$ was considerably soluble in dimethylsulfoxide. Conductivity data of the gold

Table 1. *Analytical data for gold(III) and platinum(II) complexes*

Compound	Color	m.p. (°C)	Analysis Found (calcd.) %			Molar Conductance in *DMSO* $Ohm^{-1}\,cm^2\,mol^{-1}$ $c = 1 \times 10^{-3}$ at 25 °C	Chemical Shifts (ppm) in d_6-*DMSO*	
			C	H	N		^{1}H	^{13}C
$PtCl_2C_6H_{12}N_4 \cdot 2\,H_2O$	yellow	240 (dec)	16.4 (16.3)	3.8 (3.6)	12.4 (12.7)			
$AuCl_3C_6H_{12}N_4$	orange	145	16.3 (16.2)	2.5 (2.7)	12.6 (12.6)	35	4.95	78.2
$C_6H_{12}N_4$							4.55	74

Table 2. *Some characteristic infrared frequencies of metal complexes with hexamethylenetetramine*

hmta	Vibration Type	$PtCl_2(hmta) \cdot 2\,H_2O$	$AuCl_3(hmta)$
1 238 vs	CN stretch	1 260 vs 1 235 vs 1 215 sh	1 265 vs 1 230 vs
1 009 vs	CN stretch	1 030 vs 990 vs	1 020 vs 995 vs
812 vs	CH_2 rock.	825 s 760 vs	820 s 750 vs
672 vs	CNC def.	690 s 640 ms	710 m 640 s
511 vs	skel. def.	530 ms 510 m	540 m 505 ms
	Pt—Cl	325 s	
	Au—Cl		350 s
	Au—N		305 w

compound suggested a 1:1 electrolyte but the conductivity values are increasing with time indicating an interaction with the solvent.

Infrared data of $PtCl_2(hmta) \cdot 2\,H_2O$ and $AuCl_3(hmta)$ are recorded in Table 2. Hexamethylenetetramine has T_d symmetry and only the fundamentals of the triply degenerate state T_2 are infrared active[19]. Gold and platinum 1:1 complexes usually exhibit tetragonal structures reducing the T_d symmetry of hexamethylenetetramine to effectively C_{3v}. Thus the fundamentals T_2 will transform to the totally symmetric A_1 and the degenerate E, resulting in the splitting of these bands. At the same time, the inactive fundamentals A_1 and E of the T_d symmetry turn out to be active or enhanced in intensity. From a number of complexes prepared so far[20–23] the bands that appear to be most sensitive to the nature of the bonding are those derived from the T_2—CH_2 rocking and the T_2—CNC deformation modes. Thus, the infrared spectra of $(hmta) \cdot 2\,Br_2$ (Ref.[24]) whose crystal structure is known[25] showed appreciable splitting of the bands around 1 240 cm^{-1}, 1 010 cm^{-1}, 812 cm^{-2}, 670 cm^{-1} and 511 cm^{-1}. Similar was the case for $(hmta) \cdot Br_2$ and $(hmta) \cdot I_2$ and in a number of other complexes[20,21,26], although in some cases, the most convenient criterion used was the splitting of the bands around 1 250 cm^{-1} and 1 010 cm^{-1} (Ref.[24,26]), and in other cases the splitting of the band around 511 cm^{-1} (Ref.[7]).

From Table 2 we observe that the bands around 1 250 cm^{-1} and 1010 cm^{-1} exhibit appreciable splitting and are in general agreement with previously published data on similar complexes (Fig. 1).

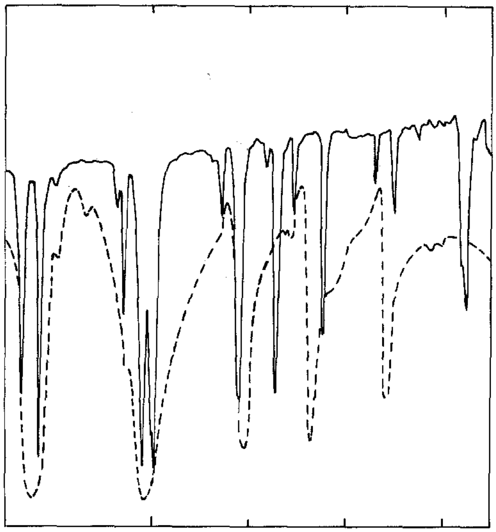

Fig. 1. Infrared spectra of *hmta* (broken line) and its 1:1 complex with gold trichloride (solid line)

Hexamethylenetetramine exhibits a sharp singlet in its ^{1}H NMR spectrum, indicating the equivalence of all the protons in this molecule, which is to be expected from a consideration of its molecular model. Similarly, a single resonance was found for all carbon atoms[27]. The ^{1}H and ^{13}C NMR peaks of the gold complex shift to considerably lower frequencies (0.4 ppm and 0,42 ppm respectively) indicating that there is an appreciable interaction of the metal ion with the nitrogen of the ligand. Similar results were obtained from infrared data for various pyridine and substituted pyridine complexes with gold trichloride[28]. Although the possibility of polymeric structures, where hexamethylenetetramine is acting as a bridging ligand, cannot be excluded, the data presented strongly suggest that the gold and platinum are interacting directly with a single nitrogen of the ligand.

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