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Rhodium(III), Palladium(II) and Platinum(II) Complexes of Bis(*o*-aminobenzenesulfonyl)ethylenediamine

Short Communication

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New complexes of the formulae $K_3[RhL_3] \cdot 2\,H_2O$, $[PdL] \cdot H_2O$ and $[M(LH_2)Cl_2]$ [where M = Pd, Pt and LH_2 = bis(*o*-aminobenzenesulfonyl)-ethylenediamine] have been prepared and characterized by conductivity measurements, thermogravimetric analysis, X-ray powder patterns and IR, Ligand Field and ^{1}H-NMR spectroscopy.

[Keywords: Bis(o-aminobenzenesulfonyl)ethylenediamine; Metal-sulfadrug interactions; Palladium(II) complexes; Platinum(II) complexes; Rhodium(III) complexes]

Rhodium(III), Palladium(II)- und Platin(II)-Komplexe mit Bis(o-aminobenzolosulfonyl)ethylendiamin (Kurze Mitteilung)

Neue Komplexe der allgemeinen Formeln $K_3[RhL_3] \cdot 2\,H_2O$, $[PdL] \cdot H_2O$ und $[M(LH_2)Cl_2]$ mit M = Pd, Pt und LH_2 = Bis(*o*-aminobenzolosulfonyl)-ethylendiamin wurden dargestellt und mit Konduktionsmessungen, thermogravimetrischen Analysen, Röntgenstrukturanalysen, IR, Ligandfeld- und ^{1}H-NMR-Spektroskopie charakterisiert.

Introduction

The interactions of metal ions with ligands containing the —SO_2—NH— grouping lead to products with interesting chemical, structural, pharmaceutical or biological properties[1—10]. The present communication describes some new deprotonated and non-deprotonated complexes of bis(*o*-aminobenzenesulfonyl)ethylenediamine (LH_2, see formula) with Rh(III), Pd(II) and Pt(II).

Experimental

LH_2 was prepared as described previously[11]. Analyses and physicochemical measurements were carried out by published methods[12,13]. All the complexes gave satisfactory elemental analyses. For the preparation of $K_3[RhL_3]\cdot 2H_2O$, to a solution of 1.35 mmol of $RhCl_3\cdot 3H_2O$ in aqueous ethanol (30 ml) were added dropwise, under vigorous stirring, 4.10 mmol of LH_2 previously dissolved in boiling 96% ethanol (85 ml). To the solution obtained, 8.2 ml (8.2 mmol) of an aqueous standard 1 *N* KOH solution were added at 50 °C; when the addition of alkali solution was completed, a golden yellow precipitate was obtained. The deprotonated palladium(II) complex precipitated immediately on adding a warm solution of $K_2[PdCl_4]$ in aqueous sodium acetate to a hot equimolar solution of the ligand in 96% ethanol. For the precipitation of $[Pd(LH_2)Cl_2]$ to a solution of lithium tetrachloropalladate(II), prepared *in situ* from 1 mmol of palladium chloride and 2 mmol of lithium chloride in 30 ml of methanol, 1 mmol of LH_2 in 30 ml of hot ethanol was added. The complex $[Pt(LH_2)Cl_2]$ was prepared by mixing a *DMF* solution of LH_2 (1 mmol in 30 ml) and a *DMF* solution of $K_2[PtCl_4]$ (1.1 mmol in 15 ml) and heating in the dark at 65° overnight; the brown solution was evaporated to dryness under reduced pressure and the residue was washed with boiling ethanol and water. All the microcrystalline products obtained were suction-filtered, washed with hot ethanol and ether and dried in air.

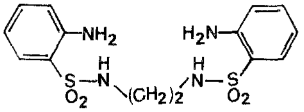
Results and Discussion

Table 1 gives some important features of the complexes. They are diamagnetic crystalline solids, insoluble in nonpolar solvents, while they are decomposed by mineral acids. The X-ray powder patterns reveal that $[Pd(LH_2)Cl_2]$ and $[Pt(LH_2)Cl_2]$ are isomorphous; the small number of the diffraction lines observed suggests polymeric structures for these compounds. Thermogravimetric studies (TGA) show that the water molecules present in the deprotonated complexes are held in the lattice. From the Λ_M values obtained, it is concluded that the Pd(II) and Pt(II)

Table 1. *Colors, yields, Λ_M values, ligand field diffuse reflectance maxima and*
sulfonyl)ethy-

Complex	Color	Yield[a] (%)	Λ_M[b] ($S\,cm^2\,mol^{-1}$)
$K_3[RhL_3]\cdot 2H_2O$	golden yellow	73	97
$[PdL]\cdot H_2O$	yellow	76	5
$[Pd(LH_2)Cl_2]$	dark yellow	81	2
$[Pt(LH_2)Cl_2]$	orange-yellow	93	7

[a] Based on the metal.
[b] Values for molar conductance for ca. 10^{-3} *M* solutions in *DMSO* at 25 °C.



complexes are non-electrolytes; $K_3[RhL_3] \cdot 2\,H_2O$ behaves in *DMSO* as a 3 : 1 electrolyte[14]. Square planar structures for the Pd(II) and Pt(II) complexes and an octahedral configuration for the Rh(III) complex are assigned on the basis of their electronic d-d diffuse reflectance spectra[15]. Comparison of the ^{1}H-NMR spectra in *DMSO-d*$_6$ of LH_2 and the non-deprotonated complexes shows that the amide protons (δ 9.63 ppm relative to Me_4Si) are almost unaffected, whereas the disappearance of this peak in the spectra of $K_3[RhL_3] \cdot 2\,H_2O$ and $[PdL] \cdot H_2O$ provides conclusive evidence that the amide protons are lost during complexation. The spectra of the Pd(II) and Pt(II) complexes show a characteristic downfield shift of the NH_2 doublet resonance relative to the free ligand (6.1 ppm), indicating binding through the amino nitrogens[16]. The frequencies of the $\nu(SO_2)$ and $\nu(NH_2)$ bands in the IR spectra confirm[9,10] that a) there is no interaction between the sulfonyl groups and the metal ions, and b) the —NH_2 groups are coordinated to Pd(II) and Pt(II) in their complexes, while they remain uncoordinated in $K_3[RhL_3] \cdot 2\,H_2O$. The Far-IR spectra of the non-deprotonated complexes exhibit $\nu(\text{Pd-Cl})_t$ at 341 cm^{-1} and $\nu(\text{Pt-Cl})_t$ at 336 cm^{-1}. The presence of only one $\nu(M\text{-Cl})_t$ vibration (B_u under C_{2h} symmetry) in each spectrum confirms their *trans* structures[17].

From the overall data presented it is concluded that L^{2-} acts as a bidentate chelate ligand in $K_3[RhL_3] \cdot 2\,H_2O$ bonding through the deprotonated sulfonamide nitrogens, while in $[PdL] \cdot H_2O$ it shows a

diagnostic IR data of the Rh(III) and Pt(II) complexes with bis(o-aminobenzene-lenediamine

Ligand Field (nm)							IR (cm^{-1})^c			
$^1A_{1g} \rightarrow$	$^1A_{2g}$,	$^1B_{1g}$,	^1E_g	$^1A_{1g} \rightarrow$	$^1T_{1g}$,	$^1T_{2g}$	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$
					373,	341	3 425	3 355	1 314	1 149
	558,	425,	387				3 310	3 224	1 317	1 127
	485,	410,	373				3 321	3 235	1 321	1 135
	465,	392,	375				3 283	3 200	1 318	1 140

[c] The $\nu_{as}(NH_2)$, $\nu_s(NH_2)$, $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ bands in the spectrum of LH_2 appear at 3 458, 3 362, 1 323 and 1 162 cm^{-1}, respectively.

tetradentate behavior with the participation of the —NH_2 groups in coordination. In [$M(LH_2)Cl_2$] the ligand bonds through the aromatic amino-N atoms alone in a *trans*-bidentate, possibly bridging, function; although it is difficult to decide on a monomeric or polymeric structure, the general insolubility and the X-ray pattern of these complexes are in agreement with polymeric units. The work herein reported seems to indicate that the amide hydrogen of sulfonamides is more acidic than an amide (peptide) hydrogen and that Pd(II) and Rh(III) promote the sulfonamide deprotonation.

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