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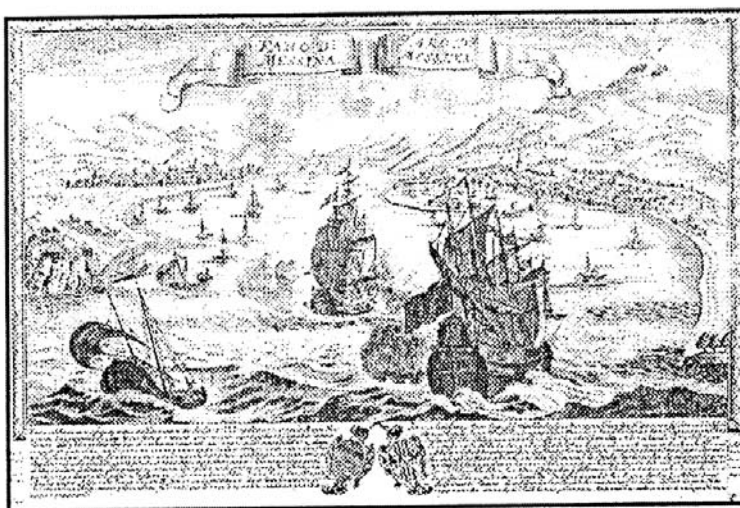
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Classe I di Scienze Fisiche  
Matematiche e Naturali

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



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**SYNTHESIS AND REACTIVITY  
OF SOLVATED CATIONS OF PLATINUM(II)**

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Reactions of solvated homoleptic metal ions are fundamental for understanding of both complex formation reactions and many inner-sphere redox processes. Such complexes are also the natural starting materials for thermodynamic studies of complex formation and for synthetic coordination chemistry.

In the case of platinum(II), the tetraaqua cation was not prepared until 1976.<sup>1</sup> Since then, it has been used both as starting material for synthesis of other solvento complexes and for various reactivity studies.

A number of organic solvates, including those of the ambidentate dimethyl sulfoxide,<sup>2</sup> propionitrile,<sup>3</sup> and various monodentate and bidentate thioethers,<sup>4</sup> have been prepared and characterized both as solid compounds and in solution by use of EXAFS and LAXS.<sup>5</sup> The tetraaqua cation itself has so far eluded all attempts at crystallizing in well-defined solid compounds.<sup>6</sup>

Since the first investigation of a square-planar solvent exchange in 1982,<sup>7</sup> a variety of such reactions have been studied.<sup>8-11</sup> In spite of the fact that those processes are chemically simple, reactivity comparisons are hampered, since

the contributions from the entering and leaving groups, *trans*- and *cis*-ligands, and stereochemistry are not separable.<sup>12</sup> This limitation also refers to activation volumes.<sup>12</sup> A comparison between analogous platinum(II) and palladium(II) exchange processes indicates that for exchange of strongly interacting ligands like olefins or carbon monoxide the two metal centers approach each other in reactivity.<sup>13,14</sup>

Kinetic studies of reversible complex formation reactions of solvento complexes of palladium and platinum indicate five-coordinate transition states with less orbital overlap, weaker and longer metal-ligand bonds, and less extensive solvation in the case of palladium(II).<sup>12</sup> This is in accord with the observed weaker *trans*- and entering ligand effects in substitution at palladium(II) centers compared to those of platinum(II).

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