Dinuclear Complex of Methionine *S*-Oxide with Platinum(II) Involving Imido-bridging; *X*-Ray Crystal Structure of Di-μ[(2*S*,S*S*)-2-amino-4-methylsulphinylbutanoato(−2)-*S*,*O*-μ-*N*]diplatinum(II)

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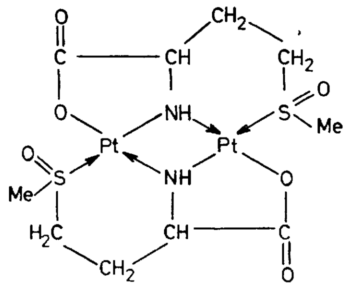
Summary The product of controlled addition of base to a dilute aqueous solution of dichloro[(2*S*,S*S*)methionine *S*-oxide]platinum(II) is shown to be the novel dinuclear complex di-μ-[(2*S*,S*S*)-2-amino-4-methylsulphinylbutanoato(−2)-*S*,*O*-μ-*N*]diplatinum(II) (I), a molecule involving five fused rings in varied conformations and the first case of a double imido-bridge in co-ordination compounds.

METHIONINE and its *S*-oxide are both potential tridentate ligands. When treated with K_2PtCl_4 in water, these ligands form complexes involving only the nitrogen and sulphur atoms as donors, dichloro(methionine)platinum(II)[1,2] and dichloro(methionine *S*-oxide)platinum(II),[3] respectively. When Volshtein[4] treated the former of these compounds with 1 mol of base he isolated an amorphous, insoluble compound analysing as Pt(methionine)Cl. Careful addition of an excess of base to the (2*S*,S*S*) diastereoisomer of the latter compound gives, in dilute solution, the slightly water-soluble crystalline compound (I), the *X*-ray crystal structure of which is reported here. The formation of (I) involves the neutralization of the carboxylic acid group and one of the amino-protons of the ligand. Its unique structure is of interest with respect both to bonding theory and the nature of the interaction of platinum(II) in biological systems.



(I)

The structure of (I) consists of discrete molecules. Each molecule comprises a system of a single four-membered, two five-membered, and two six-membered rings (Figure). All the rings are non-planar and no two rings have the same conformation. Co-ordination about the platinum atoms is nearly planar. The best least-squares planes defined by atom Pt and its donors and atom Pt′ and its donors intersect at an angle of 129·59(3)°. The bond angles about the bridging nitrogen atoms are severely distorted from tetrahedral; ∠Pt–N–Pt′ and ∠Pt–N′–Pt′ are 88·9(3) and 89·1(3)°, respectively. ∠Pt–N–C(2) and ∠Pt′–N′–C(2′) are 128·7(6) and 124·4(7)°, and ∠Pt′–N–C(2) and ∠Pt–N′–C(2′) are 111·2(6) and 107·3(6)°, respectively.

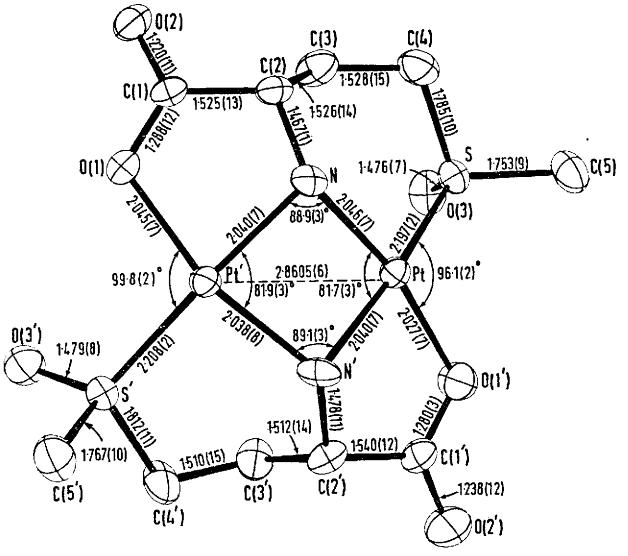


FIGURE. Perspective view of the molecule of (I). Hydrogen atoms are omitted. The central four-membered ring is puckered with the nitrogen atoms displaced toward the viewer and the platinum atoms away from the viewer. Interatomic distances are in Å. E.s.d.'s are shown in parentheses.

The puckering of the Pt_2N_2 bridge system means that the two nitrogen atoms are exposed on the same side of the molecule (the top in the Figure). The molecule thus has a nitrogen side and an oxygen side. Molecules are hydrogen-bonded from nitrogen side to oxygen side along a crystal axis. The atom N is hydrogen-bonded [*d* 2·899(10) Å] to the atom O(2) of a neighbour; the atom N′ is hydrogen-bonded [*d* 3·087(11) Å] to atom O(3′) of the same neighbour. The great differences in conformation between the two ligands are associated with the fact that non-corresponding oxygen atoms are involved in hydrogen-bonding. The six-membered ring in the primed ligand is in a symmetrical boat conformation. For the unprimed ligand, the conformation of the six-membered ring is skew-boat. The five-membered ring in the unprimed ligand is nearly flat; the dihedral angle between the planes N–C(2)–C(1) and O(1)–C(1)–C(2) is 3·4(5)°. For the primed ligand the corresponding angle is 24·7(5)°.†

The Pt–O, Pt–N, and Pt–S bond distances in (I) are all quite comparable to those found in other platinum complexes[2,5] and in the precursor of (I).[3] Other bond distances are unexceptional.

The question of the platinum–platinum interaction is interesting. The distance between the platinum atoms is within limits usually quoted for platinum–platinum bonds[5,6] and fairly close to 2·78 Å, the platinum–platinum distance in the metal.[7] However the Pt–Pt′ vector forms an angle of *ca.* 25° to both the best least-squares planes of co-ordination. This low angle means that overlap of the d_{z^2} orbitals on the platinum atoms is possible but limited. Stability gained from such interaction would tend to compensate for the ring strain at the nitrogen atoms.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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