



A New Example of Stereoisomerism in Inorganic Chemistry: Pt-Ru Chiral Axis in $[(\eta^6\text{-}p\text{-Cymene})\text{RuCl}(\mu\text{-N,N}'\text{-dialkyldithiox-amidato N,N}'\text{-Ru-S,S}'\text{Pt})\text{Pt}(2\text{-diphenylphosphinopyridine})\text{Cl}]$

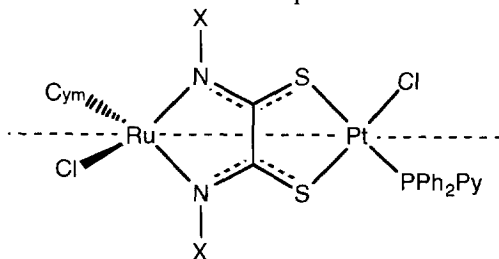
Santo LANZA,* Giuseppe Bruno, Francesco Nicolò and Rosario Scopelliti

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Vill. S. Agata, Salita Sperone 31, I-98166 Messina, Italy

Abstract: The novel compounds $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\mu\text{-RR-DTO N,N}'\text{Ru S,S}'\text{-Pt})(\text{RR-DTO})(\text{P-N})\text{Cl}]$ (P-N = 2-diphenylphosphino-pyridine, RR-DTO = N,N'-dialkyldithioxamidato, R = benzyl, **1**; R = (R)-(-)-2-hydroxypropyl (coming from (R)-(-)-2-hydroxypropyl-amine), **2**;) exhibit a Pt-Ru chiral axis which is a new example of stereoisomerism in inorganic chemistry. The crystal structure of **2** is also reported.

Copyright © 1996 Elsevier Science Ltd

Chirality in inorganic chemistry is generally associated with molecules belonging to the dissymmetric group; these molecules possess simple rotational axes and retain C_n or D_n symmetry.¹ Within this wide class of compounds, particular attention has been devoted to the C_2 symmetric metal chelates because of their involvement in asymmetric catalysis. In this field, the majority of the studies are of concern to diphosphine such as chiraphos or atropisomeric BINAP,² but other C_2 symmetric chelating molecules are now growing in interest.³ As a matter of fact, chiral axes in inorganic chemistry are related to the organic chelating ligand, whose C_2 symmetry is transferred to the chelate complex.



1 X = Benzyl

2 X = (R)-2-hydroxypropyl

We describe here the novel compounds $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\mu\text{-RR-DTO N,N}'\text{Ru S,S}'\text{-Pt})\text{Pt}(\text{RR}'\text{-DTO})(\text{P-N})\text{Cl}]$ (P-N = 2-diphenylphosphino-pyridine, RR-DTO = N,N'-dialkyldithioxamidato, R = benzyl, **1**; R = (R)-2-hydroxypropyl (coming from (R)-(-)-2-hydroxypropyl-amine), **2**).⁴ Both in **1** and in **2** a dianionic rubeanate frame links the ruthenium through the nitrogens and platinum through sulphur atoms. The N,N'-coordination is unexpected in a DTO metal complex; the only precedent example is the trimetallic copper complex $\{\text{Cu}_3[\text{C}_2\text{S}_2(\text{NCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2]_2\}(\text{ClO}_4)_2$, with a central copper in a square planar CuS_4 chromophore and the terminal metals in a $\text{CuS}_2\text{N}_2\text{O}_2$ chromophores with a 4+2 coordination.⁵ Beyond this unique exception, secondary dithioxamides seem to prefer the S,S'-coordination mode in mononuclear complexes, and the N,S-bridging mode in polymetallic as well as in polymeric systems.⁶ In **2**, as well as in **1**, ruthenium is a stereogenic centre. At the same time, the plane containing platinum ligands and the one perpendicular to it are not internal reflection planes σ_v . Thus also the platinum square plane is an element of chirality. It should be noted that the only related works on square planar chiral metal complexes appear to be the classical study of Mills and Quibell⁷ and a more recent paper of Wild.⁸ The configuration of platinum

enantiomers strictly depends on the configuration of the ruthenium centre, in such a way that only a pair of enantiomers can be envisaged for the compounds **1**. The fact is that the two metals constitute a unique element of chirality, namely a chiral axis

As said above, axial chirality in metal complexes is generally referred to the chelate ligands; hence the unprecedented Pt-Ru chiral axis in the complexes **1** and **2** establishes a new example of stereoisomerism in the organometallic chemistry. Thus, the configuration of the new complexes can be easily assessed by means of the conventional CIP rules for allene type molecules,⁹ looking along the heterobimetallic chiral axis from the higher priority metal

The molecular structure of **1** and **2** was also supported by ¹H and ³¹P NMR spectroscopy.¹⁰ In **1** the benzylic -CH₂- protons are diastereotopic because of the molecular asymmetry and their resonances appear as two AB quartet in the ¹H NMR spectrum. For the same reason aromatic cymene protons, as well as isopropyl methyl groups, are represented in the spectrum as two quartets and two doublets respectively. ³¹P NMR Pt-P resonances appear as a singlet flanked by ¹⁹⁵Pt-³¹P satellites. The synthesis of **2** was achieved by using N,N'-(R)-2-hydroxypropyl-dithioxamide as bridging ligand. As expected, the use of an enantiomerically pure dithioxamide produces **2** in an equimolar diastereomeric mixture: Ra-(RR-DTO)-**2** and Sa-(RR-DTO)-**2**. Consequently, all NMR signals of **2**, including ³¹P NMR resonances, are split. We were unable to separate the mixture by fractional crystallization, after many attempts from different solvents. Further attempts will be made for this purpose; since many other enantiomerically pure N,N'-disubstituted dithioxamides are accessible. The goal is of primary importance: the contingent catalytic properties of a bimetallic chiral axis could be exploited in asymmetric synthesis. Furthermore, **1** and **2**, owing to the uncoordinated nitrogen of phosphinopyridine, could assemble other metal fragments so transferring a bimetallic chiral axis to polymetallic systems.

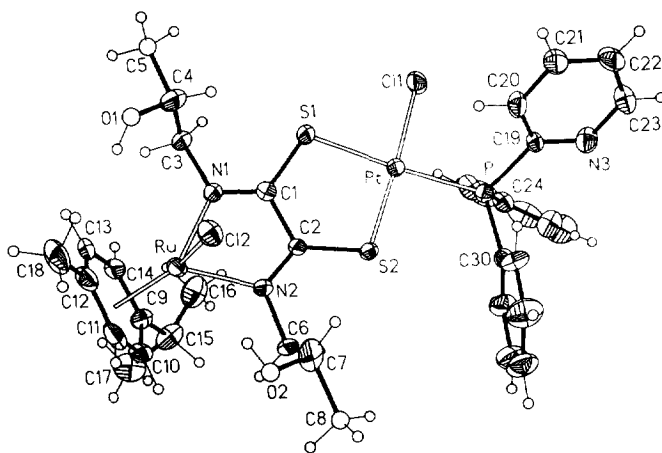


Fig 1 Perspective view of the dinuclear compound **2** revealed in the solid state by X-ray analysis. Atomic numbering scheme is reported. Atom ellipsoids are drawn at 40% of probability while hydrogen size is arbitrary. Selected bond lengths [Å] and angles [°]: Ru-N(1) 2.05(1), Ru-N(2) 2.07(1); Ru-X_{cym} 1.69(1); Ru-Cl(2) 2.425(4); Pt-S(2) 2.245(3); Pt-P 2.257(3); Pt-S(1) 2.319(3); Pt-Cl(1) 2.325(4); S(1)-C(1) 1.72(1); S(2)-C(2) 1.71(1); C(1)-N(1) 1.28(2); C(1)-C(2) 1.52(2); C(2)-N(2) 1.287(14); N(1)-C(3) 1.46(2); N(1)-Ru-N(2) 76.1(4); N(2)-Ru-X_{cym} 133.8(6); N(1)-Ru-X_{cym} 131.2(6); Cl(2)-Ru-X_{cym} 127.8(6); S(2)-Pt-P 93.6(1); S(2)-Pt-S(1) 89.5(1); P-Pt-Cl(1) 89.5(1); S(1)-Pt-Cl(1) 87.5(1); N(1)-C(1)-C(2) 115(1); N(1)-C(1)-S(1) 127(1); C(2)-C(1)-S(1) 118.2(9); N(2)-C(2)-C(1) 112(1); N(2)-C(2)-S(2) 126(1); C(1)-C(2)-S(2) 121.3(9).

Crystals for X ray analysis were grown from a mixture of all possible isomers of **2**. These were synthesized by exploiting a 2-hydroxypropyl dithioamide prepared from the racemic 1-amino-2-propanol. As expected from a polyatomic assembly with three elements of chirality, the β -carbon atoms of the two N-hydroxyalkyl substituents and the intermetallic axis, four pairs of enantiomers were obtained (three Pt-P resonancies; s, 16.43; 16.03; s (double intensity), 15.93; $J_{PP} = 3265$ Hz). The solid state X-ray determination ¹¹ revealed an average structure with undefined configuration of the two propanolic stereogenic centres, which can be attributable to the possible rotational/conformational disorder of the alkyl chains as well as to the presence of different diastereoisomers in the crystals. Both possible causes result in a large atomic displacement parameters and in an unusual geometry of the two propanol fragments.

The dinuclear unit appears quite perfectly planar with the DTO chelating *via* the S-atoms at square-planar platinum and *via* the N-atoms at tetrahedral ruthenium (Fig.1). With respect to this molecular mean plane, both propanol groups are on the same side opposite to the hindering *p*-cymene ligand which is η^6 -coordinated to the Ru atom lying on the plane. The bridging ligand is slowly distorted from planarity, as evidenced by the torsion angle S-C-C-S of 5(1)°.

References and Notes

- 1) For a review see: Harrowfield, M.J.; Wild, B.S. *Comprehensive Coordination Chemistry*, Sir Geoffrey Wilkinson Ed. **1987**, 1, 179.
- 2) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, 23, 345.
- 3) a) Togni, A.; Venanzi, L. *Angew. Chem. Int Ed Engl.* **1994**, 33, 497; b) Claver, C.; Castilon, S.; Ruitz, N.; Delogu, G.; Fabbri, S.; Gladiali, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1833.
- 4) **1** and **2** were synthesized according to the following procedure: cis-Pt(Me₂SO)(PN)Cl₂ (PN = 2-diphenylphosphino-pyridine; Arena, C.G.; Ciani, G.; Drommi, D.; Faraone, F.; Proserpio, D.M.; Rotondo, E. *J. Organomet. Chem.* **1994**, 71, 848) was reacted in chloroform with the desired DTO ligand. The stable ion pairs {Pt(PN)(Me₂SO)(H₂-R₂-DTO),Cl} (R = benzyl, R-2-hydroxypropyl) were isolated and characterized. The ion pairs were dehydrohalogenated by means of column silica gel chromatography (eluent: CHCl₃) and the neutral complexes [Pt(PN)(Me₂SO)(H-R₂-DTO)] were obtained. [Pt(PN)(Me₂SO)(H-R₂-DTO)] species was dissolved in methanol and then reacted with the stoichiometric amount of [Ru(pCy)Cl₂]₂ (pCy = 4-isopropyl-toluene). The reaction mixture was warmed at 50 °C for 0.5 h without any precaution. Then the solvent was removed and the crude product was purified by column chromatography (Al₂O₃, CHCl₃/MeOH 9:1 eluent). X ray quality crystals of **2** were obtained from MeOH.
- 5) Chauvel, C.; Girerd, J.J.; Jeannin, J.; Kahn, O.; Lavigne, G. *Inorg. Chem.* **1978**, 18, 3015.
- 6) Rosace, G.; Bruno, G.; M.Scolaro, L.; Nicolò, F.; Sergi, S.; Lanza, S. *Inorg. Chim. Acta* **1993**, 208, 59 and refs therein.
- 7) Mills, W.H.; Quibell, T.H.H. *J. Chem. Soc.* **1935**, 839.
- 8) Guger, P.; Limmer, S.O.; Watson, A.A.; Willis, A.C.; Wild, B.S. *Inorg. Chem.* **1993**, 32, 5692.
- 9) Prelog, D.; Helmchen, G. *Angew. Chem. Int Ed Engl.* **1982**, 21, 567.
- 10) ¹H and ³¹P NMR parameters for compounds **1** and **2**:
1: PN(pyridine ring) H₆,d, 8.71 ppm; H₅, t, 8.49 ppm; bz-DTO: CH₂, dd, 5.42 ppm, J = 15 Hz; dd, 4.77 ppm, J = 15 Hz; phenyl protons, m, 7.55 ppm; *p*-Cymene: CH, m, 2.91 ppm; CH₃, s, 2.16 ppm;

(CH₃)₂, d, 0.91 ppm ; d, 0.90 ppm, J = 6.84 Hz; H₂, H₃, H₅, H₆, 4d, 4.83, 4.80, 4.94, 4.66 ppm, J_{vic} = 6.05 Hz. Pt-P, s, 16.23 ppm J_{Pt-P} = 3271 Hz.

2: PN (pyridine ring): H₆, d, 8.75, d, 8.74 ppm; H₅; t, 8.51, t, 8.47 ppm; other aromatic protons: multiplets 7.94-7.25 ppm; (R)-2-hydroxypropyl-DTO: N-CH₂-CH= multiplets, 4.43-3.54 ppm; CH₃, d, 1.37, d, 1.28, d, 1.11, d 0.95 ppm; J_{vic}=6.3 Hz; *p*-cymene: H₂, H₃, H₅, H₆, four quartets, 5.55-5.11 ppm, J_{vic}=6.29 Hz; CH, m, 2.65, m, 2.64 ppm; CH₃, s, 2.22, s, 2.21 ppm; (CH₃)₂, d, 1.18, d, 1.169, d, 1.167, d, 1.144 ppm, J_{vic}=6.6Hz; P-Pt, s, 16.43, s, 16.03 ppm, J_{PtP}=3265 Hz.

- 11) Summary of crystal data for **2**: M=998.87, monoclinic, P2₁/n, a=13.4426(11), b=14.6081(13), c=20.487(2) Å, β=94.686(7)°, V=4009.6(6)Å³, Z=4, ρ_{calc}=1.655 g/cm³. The structure was solved by Patterson method, subsequently completed by a combination of least squares technique and Fourier Syntheses (SHELXTL-PLUS) and refined by the full-matrix least squares technique (SHELXL-93) based on F². The 2-hydroxypropyl fragments attached to the DTO nitrogens were found disordered, due to the possible presence of different configurations of their chiral carbon atoms in the crystal packing, and their final atoms that were refined isotropically. The H atoms were included in the refinement among the "riding model" and with a unique common fixed isotropic displacement parameter. The structure refinement, with all non-hydrogen atoms anisotropic (except the final terminal atoms of the DTO 2-hydroxypropyl fragments), reached R(F)=0.0461. Two significant residuals (about 1.2 e Å⁻³) were revealed around the inversion centre 1/2, 0, 1/2 which might suggest the presence of possible disordered solvent molecules (methanol or water): each attempt to interpret these peaks was unsuccessful.

(Received in UK 27 September 1996)