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Structure of Dichloro(3-methylsulfinylpropylamine)platinum(II), [PtCl$_2$(C$_4$H$_{11}$NOS)]

By Gwendalyn R. Champion and Luigi G. Marzilli*

Department of Chemistry, Emory University, Atlanta, Georgia 30322, *USA*

and John P. Hutchinson, Kassu Gebreyes and Jon Zubieta*

Department of Chemistry, University of New York at Albany, Albany, New York 12222, *USA*

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Abstract. $M_r = 387{\cdot}1$, monoclinic, $P2_1/c$, $a = 13{\cdot}159\ (5)$, $b = 9{\cdot}372\ (4)$, $c = 15{\cdot}468\ (3)$ Å, $\beta = 100{\cdot}99\ (2)°$, $V = 1873\ (1)$ Å^3, $F(000) = 1424$, $Z = 8$, $D_x = 2{\cdot}75$ g cm^{-3}, Mo $K\alpha$, $\bar{\lambda} = 0{\cdot}71069$ Å, $\mu = 159{\cdot}0$ cm^{-1}, room temperature, final $R = 0{\cdot}031$ for 2122 reflections. The Pt displays square-planar coordination with *cis* Cl donors. The methylsulfinylpropylamine ligand is bidentate, coordinating through the amine N and the S of the sulfoxide group. The six-membered chelate ring PtNCCCS displays a chair conformation.

Introduction. Although there is a well developed organic chemistry of compounds containing both amines and sulfoxides (Lambert & Swank, 1979), only two examples of metal complexes are known. [Pt(methionine sulfoxide)Cl$_2$] (Freeman, 1977) and [Co(ethylenediamine)$_2$(methylsulfinylethylamine)] (Gainsford, Jackson & Sargeson, 1982). This paper describes the synthesis and X-ray structure of a new amine sulfoxide metal complex, [Pt(mspa)Cl$_2$] (where mspa = 3-methylsulfinylpropylamine).

[Pt(mspa)Cl$_2$] is of interest owing to its potential as an antitumor agent, in view of *cis*-Pt(NH$_3$)$_2$Cl$_2$ and other Pt complexes which are active against tumors (Cleare & Hydes, 1980). This activity is believed to be due to their ability to bind to the nucleotide bases in DNA (Howle, Gale & Smith, 1972). Pt–dimethylsulfoxide (Me$_2$SO) complexes have also been shown to bind to nucleotides in DNA (Whiting & Ottensmeyer, 1977). Antitumor activity has been reported for the following metal–Me$_2$SO complexes: [Pt(acac)(Me$_2$SO)$_2$]$^+$ (acac = acetylacetonato) (Farrell, 1982), *cis*-[Ru$^{\text{II}}$(Me$_2$SO)$_4$Cl$_2$] (Giraldi, Sava, Bertoli, Mestroni & Zassonovich, 1977) and [RhCl$_3$(Me$_2$SO)(pur)$_2$] (pur = purine) (Giraldi *et al.*). A compound like [Pt(mspa)Cl$_2$] may react more readily as an antitumor agent than [Pt(H$_2$NCH$_2$CH$_2$NH$_2$)Cl$_2$] owing to the stronger *trans* effect of the sulfoxide.

Experimental. Potassium tetrachloroplatinate (0·24 mmol) was dissolved in water (5 ml); a solution of mspa (0·25 mmol) in water (1–2 ml) was added dropwise and the resulting orange solution heated at 323–333 K for 1 h; it turned yellow gradually; after evaporation almost to dryness, the yellow precipitate formed was collected, washed with ethanol and ether; yield, 52·5 mg (58%); recrystallization from nitromethane gave pale-yellow crystals. D_m not determined. Crystal 0·20 × 0·18 × 0·23 mm. Nicolet *R*3*m* diffractometer equipped with a highly oriented graphite monochromator (equatorial mode). Reflections $1\bar{2}\bar{8}$, $1,1,\overline{10}$, 127, 422, $35\bar{7}$, 150 and symmetry-related sets used to generate lattice parameters. Reflections in the octant $+h$, $+k$, $\pm l$ collected using a coupled θ(crystal)–2θ(counter) scan mode, $0 < 2\theta < 45°$, variable scan speed 3 to 30° min^{-1}, scan width $[2\theta(K\alpha_1) - 1{\cdot}0]$ to $[2\theta(K\alpha_2) + 1{\cdot}0]°$, backgrounds measured in the stationary-crystal–stationary-counter mode at each end of the 2θ scan range for half the time taken for the 2θ scan. Three standard reflections measured every 97 data reflections: no significant deviations over the 71 h data-collection time. A total of 2918 reflections collected; 2122 with $F_o > 6\sigma(F_o)$ used in the subsequent structure refinement. Data corrected for background, Lorentz and polarization effects and absorption ($T_{\max}/T_{\min} = 1{\cdot}23$) in the usual fashion (Bruce, Corbin, Dahlstrom, Hyde, Minelli, Stiefel, Spencer & Zubieta, 1982). Coordinates of the Pt atoms found from a three-dimensional Patterson synthesis, and a series of least-squares refinements followed by three-dimensional difference-Fourier syntheses revealed all the non-hydrogen atoms. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms with H atoms included in their idealized positions with $d(\text{C—H}) = 0{\cdot}96$ Å resulted in convergence with $R_F = 3{\cdot}09\%$ and $R_{wF} = 3{\cdot}14\%$, $w = 1/\sigma^2$, with a goodness of fit of 1·32. $(\Delta/\sigma)_{\max} = 0{\cdot}79$. Max. and min. heights on final $\Delta\rho$ map 0·4 and $-0{\cdot}5$ e Å^{-3}. No reflection affected significantly by secondary extinction. The average value of the function $\sum w(|F_o| - |F_c|)^2$ showed no major variations as a function of $|F_o|$ or $(\sin\theta)/\lambda$.

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* Authors to whom correspondence should be addressed.

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Table 1. *Positional and isotropic thermal parameters for the two independent molecules*

	x	y	z	$10^2U_{\rm iso}$(Å^2)
Pt	0·15052 (3)	0·08920 (4)	0·46696 (2)	2·41 (2)
Cl(1)	0·2788 (2)	−0·0800 (3)	0·5087 (2)	4·46 (10)
Cl(2)	0·1103 (2)	−0·0105 (3)	0·3283 (2)	4·05 (9)
N	0·2001 (6)	0·1762 (9)	0·5902 (5)	2·9 (3)
O	0·0792 (6)	0·3954 (8)	0·4084 (5)	4·3 (2)
S	0·0354 (2)	0·2600 (3)	0·4320 (2)	2·85 (8)
C(1)	0·1237 (7)	0·2122 (13)	0·6454 (6)	3·8 (4)
C(2)	0·0480 (8)	0·3301 (12)	0·6055 (6)	3·6 (4)
C(3)	−0·0284 (7)	0·2886 (11)	0·5222 (6)	3·0 (3)
C(4)	−0·0730 (8)	0·2164 (14)	0·3487 (7)	4·8 (4)
Pt′	0·53295 (3)	0·48291 (4)	0·36093 (2)	2·72 (1)
Cl(1′)	0·5354 (2)	0·7263 (3)	0·3866 (2)	4·33 (9)
Cl(2′)	0·7121 (2)	0·4804 (3)	0·3840 (2)	5·01 (11)
N′	0·5416 (6)	0·2677 (9)	0·3354 (6)	3·5 (3)
O′	0·3178 (6)	0·4920 (8)	0·2378 (5)	4·2 (3)
S′	0·3627 (2)	0·4799 (3)	0·3317 (2)	3·03 (8)
C(1′)	0·4755 (8)	0·1614 (11)	0·3701 (7)	3·5 (4)
C(2′)	0·3626 (7)	0·1875 (12)	0·3376 (7)	3·8 (4)
C(3′)	0·3199 (8)	0·3176 (13)	0·3743 (8)	4·4 (4)
C(4′)	0·3002 (10)	0·6131 (14)	0·3878 (9)	5·6 (5)

The weighting scheme is thus satisfactory and the structure complete. All calculations performed on a Nova 3 computer using local versions of *SHELTXL* programs (Sheldrick, 1978) as supplied by Nicolet XRD.

Discussion. The atomic parameters are given in Table 1,* interatomic distances and angles in Table 2. Fig. 1 is a view of the molecule and Fig. 2 shows the packing.

The two crystallographically independent molecules are identical and display a square-planar arrangement of donor atoms about the Pt. Pt—N distances are identical, within experimental error, being 2·062 (7) and 2·063 (9) Å for N and N′ respectively and are in the expected range. The Pt—S distances are crystallographically identical, 2·200 (2) and 2·204 (3) Å for S and S′. Pt—Cl distances range from 2·307 (3) for Cl(2) to 2·317 (3) Å for both Cl(1) and Cl(2′). This small variation in Pt—Cl bond distances is statistically insignificant and allows no conclusions to be made about the relative *trans* influences of S and N donors in this molecule.

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Table 2. *Interatomic distances* (Å) *and angles* (°) *for the two independent molecules*

Molecule (1)		Molecule (2)	
Pt—S	2·200 (2)	Pt′—S′	2·204 (3)
Pt—N	2·062 (7)	Pt′—N′	2·063 (9)
Pt—Cl(1)	2·317 (3)	Pt′—Cl(1′)	2·314 (3)
Pt—Cl(2)	2·307 (3)	Pt′—Cl(2′)	2·317 (3)
S—O	1·467 (8)	S′—O′	1·464 (7)
S—C(3)	1·780 (10)	S′—C(3′)	1·791 (13)
S—C(4)	1·779 (10)	S′—C(4′)	1·805 (14)
N—C(1)	1·476 (13)	N′—C(1′)	1·488 (14)
C(1)—C(2)	1·535 (15)	C(1′)—C(2′)	1·495 (14)
C(2)—C(3)	1·526 (13)	C(2′)—C(3′)	1·500 (17)
N—Pt—S	91·2 (2)	N′—Pt′—S′	92·3 (2)
Cl(1)—Pt—S	176·3 (1)	Cl(1′)—Pt′—S′	91·6 (1)
Cl(2)—Pt—S	92·4 (1)	Cl(2′)—Pt′—S′	176·8 (1)
Cl(2)—Pt—Cl(1)	90·4 (1)	Cl(2′)—Pt′—Cl(1′)	90·2 (1)
N—Pt—Cl(1)	85·9 (2)	N′—Pt′—Cl(1′)	175·6 (2)
N—Pt—Cl(2)	174·9 (2)	N′—Pt′—Cl(2′)	85·8 (2)
O—S—Pt	114·0 (3)	O′—S′—Pt′	113·9 (3)
C(3)—S—Pt	108·8 (3)	C(3′)—S′—Pt′	108·3 (3)
C(4)—S—Pt	115·5 (4)	C(4′)—S′—Pt′	115·6 (4)
C(3)—S—O	109·4 (5)	C(3′)—S′—O′	109·6 (5)
C(4)—S—O	108·5 (5)	C(4′)—S′—O′	106·8 (5)
C(4)—S—C(3)	99·7 (5)	C(4′)—S′—C(3′)	101·9 (6)
C(1)—N—Pt	119·6 (5)	C(1′)—N′—Pt′	121·8 (7)
N—C(1)—C(2)	113·2 (8)	N′—C(1′)—C(2′)	112·4 (8)
C(1)—C(2)—C(3)	115·3 (9)	C(1′)—C(2′)—C(3′)	115·2 (9)
C(2)—C(3)—S	111·5 (7)	C(2′)—C(3′)—S′	112·6 (8)

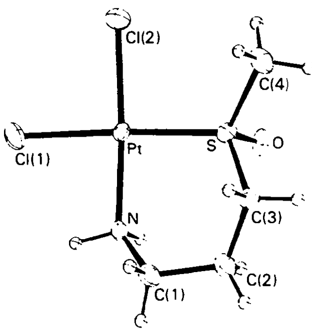

Fig. 1. Perspective view of the molecule [Pt(mspa)Cl_2], showing the atom-labeling scheme.

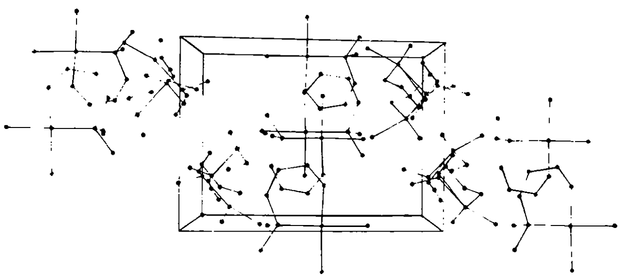

Fig. 2. Packing of the molecules in the unit cell.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39117 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of the Blue Copper(II) Complex {[7*R*(*S*),14*R*(*S*)]-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane}nitratocopper(II) Perchlorate, $[Cu(NO_3)(C_{16}H_{36}N_4)](ClO_4)$

By Tsong-Jen Lee, H. Y. Julie Lee, Chung-Shin Lee and Chung-Sun Chung

National Tsing Hua University, Hsinchu, Taiwan 300

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Abstract. $M_r = 508{\cdot}49$ (5), monoclinic, $P2_1/c$, $a = 8{\cdot}769$ (5), $b = 17{\cdot}809$ (5), $c = 14{\cdot}344$ (5) Å, $V = 2240$ (3) Å^3, $Z = 4$, $D_m = 1{\cdot}48$ (5) (by flotation in CCl_4–hexane), $D_x = 1{\cdot}51$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}187$ mm^{-1}, $F(000) = 1077{\cdot}6$, $T = 296$ (4) K. $R(F) = 0{\cdot}070$ for 1754 reflections. The central copper atom exhibits trigonal bipyramidal coordination with the four N atoms of the macrocyclic ligand and an O atom of a nitrate ion, the latter being on the equatorial plane. Thus, the four ligating N atoms of the macrocyclic ligand are not coplanar. Intramolecular hydrogen bonds are formed between the coordinated O atom and the two apical N atoms. The two non-ligating O atoms of each nitrate ion are hydrogen bonded to the two equatorial N atoms of the adjacent complex ion. The perchlorate ions are linked to the macrocyclic ligand by hydrogen bonds.

Introduction. In the blue complex $[\{Cu(tet\,b)\}_2Cl](ClO_4)_3$,* the chloride ion sits between the adjacent copper atoms and acts as a bridging atom. However, the corresponding binuclear complexes with bromide and iodide are not formed because the ionic radius of Br^- or I^- is so large that the amine groups are too far away to form hydrogen bonds with perchlorate ions (Bauer, Robinson & Margerum, 1973). In order to investigate the stabilizing effect of the hydrogen bonds and the coordination bonds around the copper atom, various atoms or ions are used to replace the chloride ion. In this work NO_3^- is used in place of Cl^- and the results are compared with our previous work on the crystal structure of $[Cu(tet\,b)(H_2O)](ClO_4)_2$ (Sheu, Lee, Lu, Liang & Chung, 1983). Detailed structures of the two isomorphous crystals are compared.

Experimental. 2 g of $[\{Cu(tet\,b)_2\}Cl](ClO_4)_3$, prepared as described by Bauer *et al.* (1973), was dissolved in hot dilute nitric acid. Silver nitrate was then added to the solution until AgCl was completely precipitated. The precipitate of AgCl was filtered off. Blue needle crystals of $[Cu(NO_3)(tet\,b)](ClO_4)$ were formed after evaporation of the solution. The crystals were dried in air at room temperature and used for X-ray work.

Experimental data and structure solution parameters are summarized in Table 1. After correction for background, Lorentz–polarization, absorption and time-decay effects, 1754 independent reflections were found with $F_o > 3\sigma(F)$.

Structure solved by heavy-atom method; full-matrix least-squares refinements (*ORFLS*; Busing, Martin & Levy, 1962) for coordinates and anisotropic temperature factors of non-hydrogen atoms; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma_F^2(I) + q|F_o|^2]^{-1}$, $\sigma_F(I) = [k/2(\mathrm{Lp})^{1/2}]\{[\sigma^2(I)_{\mathrm{counting}} + (0{\cdot}02I)^2]/I\}^{1/2}$, Lp, I, k are the Lorentz–polarization factors, reflection intensity and scale factors, respectively; the factor 0·02 is the additional error estimated for our present instrumental instability (q set to 0·001 finally). To locate the H atoms in the methyl groups, one of the highest peaks around the C atom in the methyl groups was picked up from the difference Fourier map; the

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* Abbreviation: The macrocyclic ligand, tet b, is the racemic form of [7*R*(*S*),14*R*(*S*)]-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, in which the two hydrogen atoms attached to the asymmetric carbon chiral centers are on the same side of the macrocyclic plane (Whimp, Bailey & Curtis, 1970).

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