

## References

- Bencini, A., Midollini, S. & Zanchini, C. (1989). *Inorg. Chem.* **28**, 1963–1969.
- Bencini, A. & Zanchini, C. (1991). *Inorg. Chem.* **30**, 4245–4251.
- Cornelissen, J. P., Van Diemen, J. H., Groeneveld, L. R., Haasnoot, J. G., Spek, A. L. & Reedijk, J. (1992). *Inorg. Chem.* **31**, 198–202.
- Delhaes, P. (1992). *Lower Dimensional Systems and Molecular Electronics*, edited by R. M. Metzger *et al.*, and references therein. New York: Plenum Press.
- Endres, H. (1983). *Extended Linear Chain Compounds*, edited by J. S. Miller, Vol. 3, p. 263. New York: Plenum Press.
- Hoekstra, A., Spoelder, T. & Vos, A. (1972). *Acta Cryst.* **B28**, 14–20.
- Inoue, M. & Inoue, M. B. (1986). *Inorg. Chem.* **25**, 37–41.
- Kistenmacker, T. J., Emge, T. J., Bloch, A. N. & Cowan, D. O. (1982). *Acta Cryst.* **B38**, 1193–1199.
- Lacroix, P., Kahn, O., Gleizes, A., Valade, L. & Cassoux, P. (1984). *Nouv. J. Chim.* **8**, 643–651.
- Melby, L. R., Harder, R. J., Hertler, W. R., Mahler, W., Benson, R. E. & Mochel, W. E. (1962). *J. Am. Chem. Soc.* **84**, 3374–3387.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Oshio, H., Ino, E., Mogi, I. & Ito, T. (1993). *Inorg. Chem.* **32**, 5697–5703.
- Ruiz, R., Julve, M., Cano, J., Soto, J., Martinez-Mañez, R., Muñoz, M. C. & Payá, J. (1993). *Transition Met. Chem.* **18**, 523–527.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

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### *trans*-Hydroxotrīs(isothiocyanato)bis-(triphenylphosphine)rhenium(IV) Methanol Solvate

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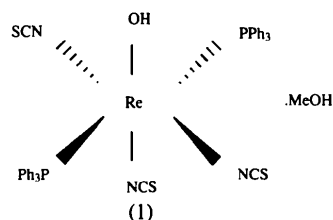
## Abstract

The title compound consists of well-separated units of [Re(OH)(NCS)<sub>3</sub>(Ph<sub>3</sub>P)<sub>2</sub>] complexes and MeOH solvent molecules. The Re atom is six-coordinate in a distorted octahedral coordination sphere. The two triphenylphosphine ligands are arranged *trans* to each other. The Re—OH distance is 2.171(4) Å and lies in the range for a single Re—O bond. The NCS ligands are coordinated *via* nitrogen.

## Comment

[Re(OH)(NCS)<sub>3</sub>(Ph<sub>3</sub>P)<sub>2</sub>].MeOH, (1), is formed by the reaction of the well known complex [ReNCI<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>]

(Chatt, Garforth, Johnson & Rowe, 1964) with trimethylsilylisothiocyanate, Me<sub>3</sub>SiNCS. In contrast to the reactions with alkali or ammonium halides or pseudo-halides (Rouschias, 1974, and references therein; Fergusson, 1966; Hübener, Abram & Strähle, 1994*a,b*), not only does an exchange of the chloro ligand occur, but the nitrido ligand is removed and the rhenium is reduced to the Re<sup>IV</sup> oxidation state. The air-stable



compound is readily soluble in organic solvents such as acetone or CHCl<sub>3</sub>. IR studies carried out in solid KBr showed the  $\nu(\text{NCS})$  stretching vibrations for the isothiocyanate ligands at 1976, 2007 and 2050 cm<sup>-1</sup> and the OH absorption band centred at 3379 cm<sup>-1</sup>. Fast atom bombardment mass spectra of [Re(OH)(NCS)<sub>3</sub>(Ph<sub>3</sub>P)<sub>2</sub>].MeOH showed evidence for the molecular ion peak at  $m/z = 902$ . Fragmentation mainly occurs by the loss of complete ligands:  $m/z = 885$  [Re(NCS)<sub>3</sub>(Ph<sub>3</sub>P)<sub>2</sub>]<sup>+</sup>,  $m/z = 843$  [ReO(NCS)<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>]<sup>+</sup>,  $m/z = 827$  [Re(NCS)<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>]<sup>+</sup>,  $m/z = 623$  [Re(NCS)<sub>2</sub>(Ph<sub>3</sub>P)]<sup>+</sup> and  $m/z = 565$  [Re(NCS)(Ph<sub>3</sub>P)]<sup>+</sup>. The nature of the OH<sup>-</sup> ligand was verified by the recrystallization of the compound from acetone/D<sub>2</sub>O, which leads to an H/D exchange in this position. As a result, the mass spectrometric molecular ion peak shifted to  $m/z = 903$ . IR studies showed the OD absorption band at 2360 cm<sup>-1</sup>. The spectroscopic results are confirmed by the structure determination of [Re(OH)(NCS)<sub>3</sub>(Ph<sub>3</sub>P)<sub>2</sub>].MeOH. The title compound consists of discrete monomeric molecules co-crystallized with molecules of solvent methanol in a 1:1 ratio. A SCHAKAL89 plot (Keller, 1989) together with the molecular numbering scheme is shown in Fig. 1.

The Re atom is six-coordinate, the two *trans* triphenylphosphine ligands are bonded to Re in an approximately linear fashion with a P—Re—P angle of 175.35(5)°. The Re—P bond distances, 2.464(1) and 2.470(1) Å, fall in the normal range of Re—P distances observed in six-coordinate tertiary phosphine complexes (2.45–2.51 Å; Drew, Tisley & Walton, 1970; Hübener, Abram & Strähle, 1994*b*). The three NCS<sup>-</sup> ligands are nitrogen-bonded, as has been found for all structurally characterized rhenium complexes with this ligand (Hahn, Nimry, Robinson, Salmon & Walton, 1978; Carrondo, Shakir & Skapski, 1978; Conner & Walton, 1987, and references therein; Hübener & Abram, 1993; Hübener, Abram & Strähle, 1994*a,b*). The isothiocyanate ligands are almost linear [N—C—S angles from 177.2(6) to 179.4(5)°] and do not show unusual bond dis-

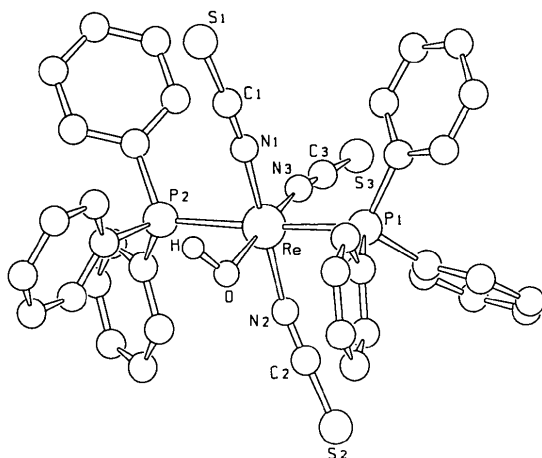


Fig. 1. SCHAKAL89 plot (Keller, 1989) of  $[\text{Re}(\text{OH})(\text{NCS})_3(\text{C}_{18}\text{H}_{15}\text{P})_2]$  along with the atomic numbering scheme.

tances. The Re—O distance is 2.171 (4) Å, which is in the typical range for Re—O single bonds (Bombieri, Mazzi, Gilli & Hernández-Cano, 1978; Conner & Walton, 1987, and references therein; Hübener & Abram, 1993).

## Experimental

### Crystal data

$[\text{Re}(\text{OH})(\text{NCS})_3(\text{C}_{18}\text{H}_{15}\text{P})_2] \cdot \text{CH}_4\text{O}$

$M_r = 934.08$

Monoclinic

$P2_1/c$

$a = 9.976$  (4) Å

$b = 29.601$  (6) Å

$c = 14.189$  (5) Å

$\beta = 107.74$  (2)°

$V = 3990.9$  (9) Å<sup>3</sup>

$Z = 4$

$D_x = 1.555$  Mg m<sup>-3</sup>

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega$  scans

Absorption correction: refined from  $\Delta F$  (DIFABS; Walker & Stuart, 1983)

10 287 measured reflections

9901 independent reflections

6797 observed reflections

$[I \geq 3\sigma(I)]$

### Refinement

Refinement on  $F$

$R = 0.032$

$wR = 0.036$

$S = 1.286$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 8-13^\circ$

$\mu = 3.3518$  mm<sup>-1</sup>

$T = 223$  K

Plate

$0.6 \times 0.4 \times 0.1$  mm

Brown-red

$R_{\text{int}} = 0.0882$

$\theta_{\text{max}} = 29^\circ$

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 40$

$l = -19 \rightarrow 19$

3 standard reflections

frequency: 60 min and

every 200 reflections

intensity decay: 2.5%

Extinction correction:  
Zachariasen (1963)

9719 reflections  
465 parameters  
H-atom parameters not refined  
 $w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$

Extinction coefficient:  
 $6.5466 \times 10^{-9}$   
Atomic scattering factors  
from *International Tables*  
for X-ray Crystallography  
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Re	0.13807 (2)	0.11593 (1)	0.19600 (1)	0.02177 (7)
S1	0.2038 (2)	-0.02884 (5)	0.0722 (1)	0.057 (1)
S2	-0.0095 (2)	0.26385 (5)	0.2418 (1)	0.0483 (9)
S3	0.6058 (2)	0.15413 (6)	0.3964 (1)	0.0442 (9)
P1	0.1825 (1)	0.15864 (4)	0.05947 (8)	0.0236 (6)
P2	0.0898 (1)	0.06770 (4)	0.32398 (9)	0.0253 (6)
O	-0.0827 (4)	0.1095 (2)	0.1117 (3)	0.046 (2)
O10	0.2724 (5)	0.6569 (2)	0.3019 (4)	0.077 (4)
N1	0.1710 (4)	0.0576 (1)	0.1351 (3)	0.026 (2)
N2	0.0821 (4)	0.1758 (1)	0.2394 (3)	0.028 (2)
N3	0.3401 (4)	0.1252 (1)	0.2802 (3)	0.029 (2)
C1	0.1853 (5)	0.0215 (2)	0.1065 (4)	0.027 (2)
C2	0.0422 (5)	0.2127 (2)	0.2410 (3)	0.030 (3)
C3	0.4513 (5)	0.1372 (2)	0.3293 (4)	0.029 (2)
C10	0.3391 (8)	0.6946 (3)	0.3639 (7)	0.075 (6)
C11	0.3002 (5)	0.1332 (2)	-0.0016 (3)	0.028 (2)
C12	0.4072 (6)	0.1043 (2)	0.0511 (4)	0.031 (3)
C13	0.5054 (6)	0.0882 (2)	0.0081 (4)	0.037 (3)
C14	0.5006 (6)	0.1012 (2)	-0.0863 (4)	0.040 (3)
C15	0.3952 (6)	0.1297 (2)	-0.1394 (4)	0.041 (3)
C16	0.2951 (5)	0.1459 (2)	-0.0977 (4)	0.033 (3)
C21	0.2549 (5)	0.2156 (2)	0.0844 (4)	0.027 (2)
C22	0.3254 (6)	0.2294 (2)	0.1798 (4)	0.030 (3)
C23	0.3923 (7)	0.2708 (2)	0.1968 (5)	0.041 (3)
C24	0.3906 (7)	0.2988 (2)	0.1190 (5)	0.047 (4)
C25	0.3190 (7)	0.2858 (2)	0.0229 (5)	0.045 (3)
C26	0.2517 (6)	0.2445 (2)	0.0060 (4)	0.037 (3)
C31	0.0163 (5)	0.1667 (2)	-0.0390 (3)	0.029 (2)
C32	-0.0709 (6)	0.2024 (2)	-0.0317 (4)	0.039 (3)
C33	-0.2048 (6)	0.2057 (3)	-0.0989 (5)	0.052 (4)
C34	-0.2500 (7)	0.1740 (3)	-0.1722 (5)	0.055 (5)
C35	-0.1659 (7)	0.1381 (2)	-0.1789 (5)	0.047 (4)
C36	-0.0312 (6)	0.1341 (2)	-0.1122 (4)	0.037 (3)
C41	-0.0864 (5)	0.0426 (2)	0.2807 (3)	0.030 (2)
C42	-0.1951 (6)	0.0558 (2)	0.3155 (4)	0.038 (3)
C43	-0.3270 (6)	0.0372 (2)	0.2785 (5)	0.050 (4)
C44	-0.3535 (7)	0.0047 (2)	0.2047 (5)	0.044 (3)
C45	-0.2455 (6)	-0.0089 (2)	0.1694 (4)	0.041 (3)
C46	-0.1129 (6)	0.0094 (2)	0.2072 (4)	0.036 (3)
C51	0.2017 (5)	0.0178 (2)	0.3600 (3)	0.028 (2)
C52	0.1511 (6)	-0.0206 (2)	0.3962 (4)	0.040 (3)
C53	0.2371 (7)	-0.0585 (2)	0.4253 (5)	0.043 (3)
C54	0.3710 (7)	-0.0583 (2)	0.4176 (5)	0.044 (3)
C55	0.4209 (7)	-0.0204 (2)	0.3811 (5)	0.051 (3)
C56	0.3360 (6)	0.0172 (2)	0.3522 (4)	0.038 (3)
C61	0.0953 (5)	0.0947 (2)	0.4406 (3)	0.031 (3)
C62	0.0232 (6)	0.1352 (2)	0.4380 (4)	0.035 (3)
C63	0.0178 (6)	0.1550 (2)	0.5259 (4)	0.047 (3)
C64	0.0855 (7)	0.1352 (2)	0.6163 (4)	0.053 (4)
C65	0.1589 (8)	0.0957 (2)	0.6187 (4)	0.050 (4)
C66	0.1645 (6)	0.0750 (2)	0.5314 (4)	0.038 (3)
H	-0.110 (6)	0.076 (2)	0.101 (4)	

Table 2. Selected geometric parameters (Å, °)

Re—P1	2.464 (1)	N2—C2	1.164 (7)
Re—P2	2.470 (1)	N3—C3	1.170 (6)
Re—N1	2.002 (4)	O—H	1.03 (6)
Re—N2	2.011 (4)	C1—S1	1.595 (5)
Re—N3	2.024 (4)	C2—S2	1.600 (6)
Re—O	2.171 (4)	C3—S3	1.625 (5)
N1—C1	1.169 (7)	O10—C10	1.45 (2)

P1—Re—P2	175.35 (5)	N1—Re—O	87.6 (2)
P1—Re—N1	90.7 (1)	N2—Re—N3	91.1 (2)
P1—Re—N2	85.5 (1)	N2—Re—O	85.3 (2)
P1—Re—N3	90.5 (1)	N3—Re—O	176.2 (2)
P1—Re—O	90.4 (1)	Re—N1—C1	173.3 (4)
P2—Re—N1	85.0 (1)	Re—N2—C2	163.9 (4)
P2—Re—N2	98.6 (1)	Re—N3—C3	170.0 (5)
P2—Re—N3	91.5 (1)	N1—C1—S1	177.2 (6)
P2—Re—O	87.8 (1)	N2—C2—S2	178.4 (6)
N1—Re—N2	171.8 (1)	N3—C3—S3	179.4 (5)
N1—Re—N3	96.1 (1)	Re—O—H	111 (3)

The positions of the H atoms on the phenyl rings were calculated and were included in the structure-factor calculations. Cell refinement: *SET4* (de Boer & Duisenberg, 1984). Data reduction: *SDP* (Enraf-Nonius, 1985). Program used to solve structure: *SHELXS86* (Sheldrick, 1985). Program used to refine structure: *SDP*. Molecular graphics: *SCHAKAL89* (Keller, 1989). Software used to prepare material for publication: *SDP*, *UTABLE* (Kretschmar, 1989). Programs were run on a DEC VAX Station 3100.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: KA1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
- Bombieri, G., Mazzi, U., Gilli, G. & Hernández-Cano, F. (1978). *J. Organomet. Chem.* **159**, 53–62.
- Carrondo, C. T. de M. A. A., Shakir, R. & Skapski, A. C. (1978). *J. Chem. Soc. Dalton Trans.* pp. 841–848.
- Chatt, J., Garforth, J. D., Johnson, N. P. & Rowe, G. A. (1964). *J. Chem. Soc.* pp. 1012–1020.
- Conner, K. A. & Walton, R. A. (1987). Editors. *Comprehensive Coordination Chemistry*, Vol. 4, 1st ed., pp. 125–213. Oxford: Pergamon Press.
- Drew, M. G. B., Tisley, D. G. & Walton, R. A. (1970). *Chem. Commun.* pp. 600–601.
- Enraf-Nonius (1985). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- Fergusson, J. (1966). *Coord. Chem. Rev.* **1**, 459–503.
- Hahn, J. E., Nimry, T., Robinson, W. R., Salmon, D. J. & Walton, R. A. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1232–1236.
- Hübener, R. & Abram, U. (1993). *Inorg. Chim. Acta*, **211**, 121–123.
- Hübener, R., Abram, U. & Strähle, J. (1994a). *Inorg. Chim. Acta*, **216**, 223–228.
- Hübener, R., Abram, U. & Strähle, J. (1994b). *Inorg. Chim. Acta*, **224**, 193–197.
- Keller, E. (1989). *SCHAKAL89. Fortran Program for the Graphic Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.
- Kretschmar, M. (1989). *UTABLE. Program for Calculation of U<sub>eq</sub>*. Univ. of Tübingen, Germany.
- Rouschias, G. (1974). *Chem. Rev.* **74**, 531–566.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

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## Chlorure de *cis*-Chloro(diméthyl sulfoxyde)(metformine)platine(II)

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## Abstract

In this *cis*-chloro(dimethyl sulfoxide)(metformin)platinum(II) chloride complex (metformin is 1,1-dimethylbiguanide), [PtCl(C<sub>4</sub>H<sub>11</sub>N<sub>5</sub>)(C<sub>2</sub>H<sub>6</sub>OS)]Cl, the coordination about the Pt atom is square planar, involving Cl, S and two N atoms. The N atoms are in *cis* positions and belong to the metformin ligand. In the complex cation, the metformin–Pt ring is approximately planar. There is a delocalized orbital over the biguanide group. An N—H···O intramolecular hydrogen bond [2.75 (1) Å] forms a pseudo five-membered ring. Several N—H···Cl intermolecular hydrogen bonds take part in the cohesion of the structure.

## Commentaire

La synthèse et l'étude structurale des composés de coordination formés par le platine(II) et la metformine (1,1-diméthylbiguanide) ont été entreprises dans la perspective d'obtenir des produits possédant une activité antitumorale.

L'unité asymétrique de (I) contient un anion Cl<sup>−</sup> et un cation *cis*-chloro-*S*-(diméthyl sulfoxyde)(metformine)-platine(II). L'atome de platine a un environnement de type plan-carré constitué par Cl(1), S, N(2) et N(4). S appartient à la molécule de diméthyl sulfoxyde, N(2) et N(4) à la molécule de metformine qui se comporte donc comme un coordinaat bidentate.

