metal-organic compounds

Diammonium hexakis(thiocyanato-κN)-rhenate(IV) dimethyl sulfone tetrasolvate

Andrzej Kochel[a]* and Małgorzata Hołyńska[b]

[a]Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie Street, 50-383 Wrocław, Poland, and [b]Fachbereich Chemie der Philipps-Universitaet, Hans-Meerwein-Strasse, D-35043 Marburg, Germany

Correspondence e-mail: garfild9@gazeta.pl

The title compound, $(NH_4)_2[Re(NCS)_6] \cdot 4C_2H_6O_2S$, was obtained by solvothermal synthesis as part of a project on rhenium thiocyanate catalysts and starting materials for further aggregation to molecular magnets. The compound is the ammonium salt of octahedral hexakis(thiocyanato-κN)-rhenate(IV) anions, which lie on centres of inversion. The dimethyl sulfone solvent molecules are involved in $R_4^2(8)$ and D N—H⋯O hydrogen-bonded motifs. N—H⋯S and S⋯S short contacts are also present. Hydrogen-bonded ammonium–dimethyl sulfone layers alternate with layers formed by the complex anion (with S⋯S short contacts) parallel to (100).
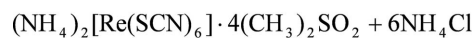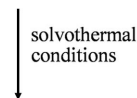
Comment

Rhenium thiocyanate complexes possess catalytic activity, which makes them an alternative to the expensive catalyst methyltrioxidorhenium (MTO) (Dinda *et al.*, 2009). Synthetic routes for the synthesis of such catalysts are still being explored, in particular through reductive thiocyanolysis (Dinda *et al.*, 2009) or ligand exchange in hexachlorido-rhenates(IV) (Gonzalez *et al.*, 2008). Synthetic difficulties arise in connection with product purification.

The title compound, (I), was obtained as part of a project on synthetic routes for providing new rhenium catalysts and reagents for further syntheses of new polynuclear materials. Compound (I) is a product of the reaction of ammonium thiocyanate and ammonium hexachloridorhenate(IV), carried out under solvothermal conditions (see reaction scheme). The solvent, dimethyl sulfone (m.p. 382 K), proves to be suitable under these conditions for ligand exchange in the hexachloridorhenate(IV) anion.

The structure of (I) contains rare centrosymmetric hexakis(thiocyanato-κN)rhenate(IV) anions (Fig. 1). To date, only a modest amount of crystal data has been reported for this anion, namely for a tetraphenylphosphonium salt (Dinda *et*

al., 2009), and for a tetrabutylammonium salt along with its linkage isomer (Gonzalez *et al.*, 2008). In both these cases, the anions are also centrosymmetric. Spectroscopic and magnetic

$$(NH_4)_2ReCl_6 + 6NH_4SCN + 4(CH_3)_2SO_2$$

$$\downarrow \text{solvothermal conditions}$$

$$(NH_4)_2[Re(SCN)_6] \cdot 4(CH_3)_2SO_2 + 6NH_4Cl$$

data for a tetraphenylarsonium salt are available (Małecka *et al.*, 2002). Reports of dimethyl sulfone are scarce in the literature; it has been observed on its own (Sands, 1963; Langs *et al.*, 1970; Fronczek, 2006, 2007), as a solvent (Bandy *et al.*, 1981; Coles *et al.*, 2003) and as a ligand (Cotton & Felthouse, 1981; Dikarev *et al.*, 2003; Biagini *et al.*, 2004), and has been observed to participate in discrete hydrogen-bonded motifs.

(I)
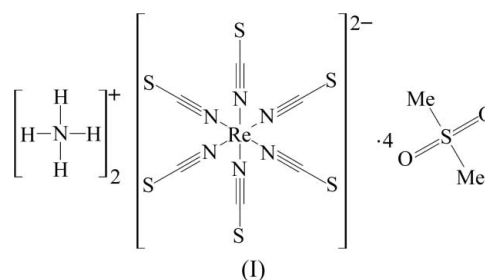
The octahedral geometry of the anion of (I) (Table 1) can be compared with those found for the tetraphenylphosphonium and tetrabutylammonium salts (Dinda *et al.*, 2009; Gonzalez *et al.*, 2008). In (I), all the Re—N bond lengths are almost equal, while in both of the previously reported structures, some
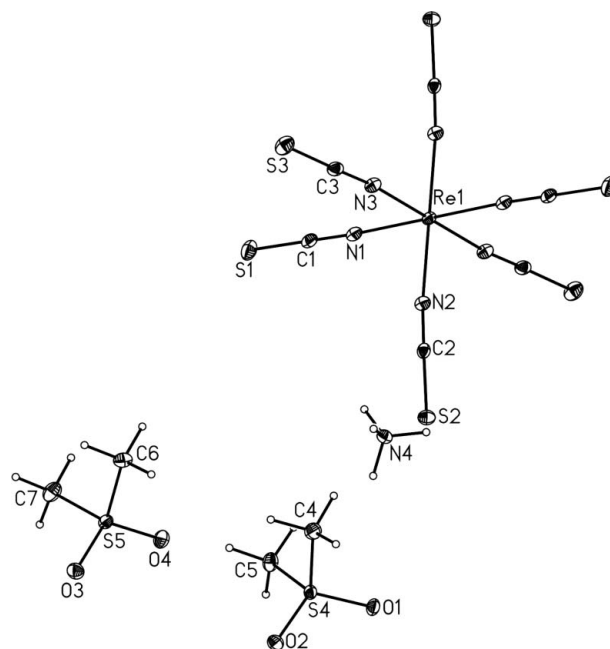
Figure 1
The components of (I), with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z$.]
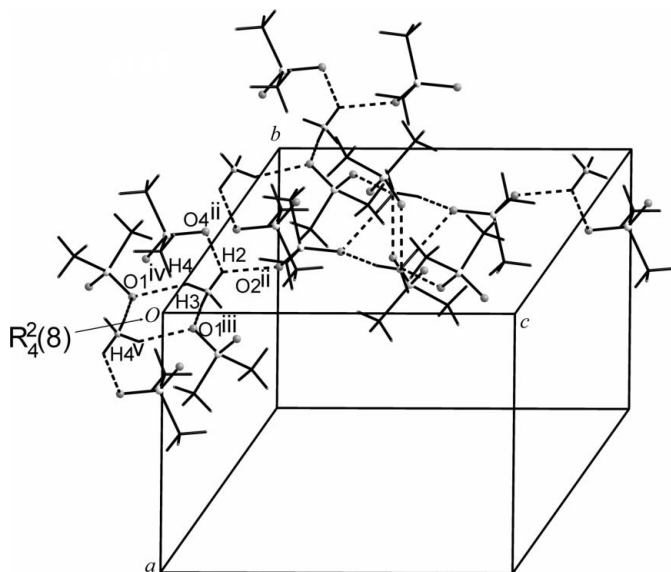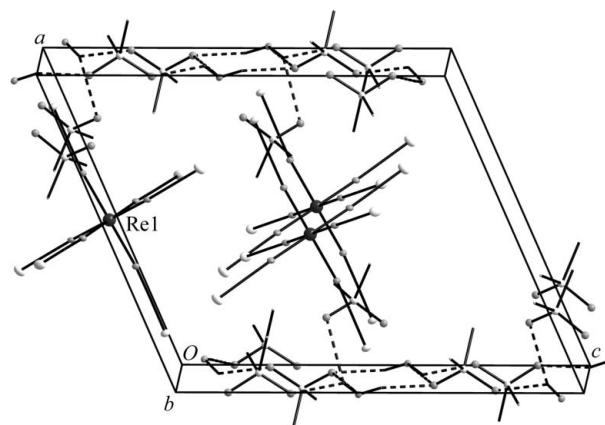
Figure 2
Hydrogen-bonded cation–solvent layers in (I), with the ring graph-set motif indicated. Hydrogen bonds are displayed as dashed lines. C and H atoms are shown as sticks for clarity. [Symmetry codes: (ii) $-x$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (iii) x, $y - 1$, z; (iv) $-x$, $-y + 1$, $-z$; (v) $-x$, $-y$, $-z$.]

Figure 3
Puckered hydrogen-bonded layers containing dimethyl sulfone molecules and ammonium cations, alternating with hexakis(thiocyanato-κN)rhenate(IV) anion layers, both parallel to (100). Hydrogen bonds are drawn as dashed lines. H atoms, except those involved in hydrogen bonding, have been omitted.

degree of anion axial distortion was observed, probably resulting from the influence of intermolecular interactions. For the tetrabutylammonium salt, the Re—N distances are 2.043 (6)/2.012 (5)/2.000 (5) and 2.045 (6)/2.016 (4)/2.155 (7) Å for the two symmetry-independent anions. The long bond is to a thiocyanate ligand involved in a short S···S contact. For the tetraphenylphosphonium salt, the Re—N distances are 2.025 (7) and 1.943 (5) Å (Re on a site of $4/m$ symmetry). All thiocyanate ligands bonded to the Re^{IV} centre in (I) are linear, with bond lengths comparable with previously observed values [*e.g.* for the tetraphenylphosphonium salt, C—N = 1.154 (10)–1.197 (11) Å and C—S = 1.604 (8)–1.607 (10) Å]. This geometry can best be understood in terms of one of the possible ligand resonance forms (see scheme).

The ammonium atoms H2–H4 participate as donors in N—H···O hydrogen bonds with dimethyl sulfone O atoms (Table 2). This does not seem to affect the S—O bond lengths, which, along with other molecular parameters, are as expected (Table 1). They are also comparable with, for example, the values found for 1,4,7,10,13,16-hexaoxacyclooctadecane bis-(dimethyl sulfone) (Bandy *et al.*, 1981), where the relevant S—O bond lengths are 1.439 (2) and 1.440 (2) Å. The remaining H atom is involved in an N4—H1···S1^{vi} short contact [N···S = 3.551 (3) Å and N—H···S = 170°; symmetry code: (vi) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$]. N4—H3···O1^{iii} and N4—H4···O1^{iv} hydrogen bonds participate in $R_4^2(8)$ graph-set motifs (Etter *et al.*, 1990), whereas the bifurcated N4—H2···O2^{ii} and N4—H2···O4^{ii} hydrogen bond constitutes two *D* graph-set motifs (Fig. 2; symmetry codes as in Table 2). These motifs all occur within hydrogen-bonded layers formed by dimethyl sulfone molecules and ammonium cations parallel to (100), alternating with anion layers with interanion S···S short contacts (Fig. 3). It has been shown that such S···S

contacts can dominate crystal structure packing in thiocyanate complex salts, even in the presence of hydrogen bonds (Jana *et al.*, 2007). In (I), all thiocyanate S atoms are involved in such contacts, of which two types are present, *viz.* S1···S3^{vii} of 3.4696 (15) Å within the anion layer (Fig. 3) and an interlayer S2···S2^{iv} contact of 3.5716 (16) Å [symmetry codes: (iv) $-x$, $-y + 1$, $-z$; (vii) x, $y + 1$, z]. We note that the C—S bond for the thiocyanate ligand involved in the latter contact, *viz.* S2···S2^{iv}, is slightly longer than those in the other thiocyanate ligands (Table 1). Similar S···S contacts [but longer, at 4.114 (4) Å] were observed for the tetrabutylammonium salt (Gonzalez *et al.*, 2008).

Compound (I) will be used as a starting material in reactions with amines, with possible further aggregation to products of interest for their magnetic and/or catalytic properties.

Experimental

The synthesis of the title compound was carried out in a Berghoff BF-100 autoclave under a nitrogen atmosphere. A 150 ml Teflon vessel was charged with $(NH_4)_2ReCl_6$ (1.20 g) [prepared according to Watt & Thompson (1963)], dimethyl sulfone (15 g) and NH_4SCN (3.50 g). The vessel was sealed under nitrogen at a primary pressure of 0.5 bar (1 bar = 100 000 Pa). The reaction was carried out at 393 K. During the reaction, the pressure rose to 3.5 bar. After 20 h of continuous stirring and heating at 393 K, the reaction mixture was cooled to room temperature and extracted with distilled water in order to remove part of the solvent. The remaining solid product (4.50 g) was dried over P_4O_{10} in a desiccator. The solid was dissolved in acetonitrile (100 ml) and concentrated on a rotary evaporator. From the cooled solution, a red–brown precipitate (2.01 g) was obtained, which was soluble in acetone, acetonitrile, dimethylformamide and chloroform. Product homogeneity was checked by means of thin-layer chromatography on a silica-gel-coated plate (0.2 mm layer) using dichloromethane as the developing solvent, and the product was found to be a mixture of different compounds. Separation was carried out using column chromatography on a column filled with silica gel 60

(0.063–0.20 mm, MN Kieselgel 60; height 50 cm, diameter 1.5 cm). The product mixture, dissolved in dichloromethane (30 ml), was introduced onto the column and the eluent used was dichloromethane–methanol–acetonitrile (20:3:2 *v/v/v*). In the course of the separation, one orange fraction and one yellow fraction were obtained (the yellow fraction appeared second, in a small quantity). Compound (I) crystallized from the first fraction (yield 75%). The yellow by-product was characterized by elemental analysis and IR spectroscopy, but the results were ambiguous. Spectroscopic analysis for the title compound, (I): IR bands (Nujol, ν, cm^{-1}): 547 (*m*), 494 (*vs*), 458 (*vs*), 301 (*vs*), 182 (*m*), 87 (*s*), 2916 (*vs*), 2844 (*vs*), 2399 (*m*), 2324 (*m*), 2259 (*m*), 2192 (*m*), 2053 (*vs*), 1641 (*s*), 1454 (*vs*), 1375 (*vs*), 1130 (*vs*), 934 (*s*), 760 (*s*), 697 (*s*), 494 (*m*), 459 (*s*). Interpretation of selected bands: 2399–2053 cm^{-1} stretching *M*–NCS modes, 934–760 cm^{-1} stretching *M*–NCS modes, and 494 and 459 cm^{-1} deformation *M*–NCS modes. Elemental analysis calculated: C 17.74, H 3.40, N 11.82, S 33.84%; found: C 17.01, H 3.20, N 11.10, S 33.56%.

Crystal data

(NH$_4$)$_2$[Re(NCS)$_6$]·4C$_2$H$_6$O$_2$S	$V = 1760.5$ (8) Å^3
$M_r = 947.28$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.128$ (3) Å	$\mu = 4.09$ mm^{-1}
$b = 9.493$ (3) Å	$T = 100$ K
$c = 15.412$ (4) Å	$0.15 \times 0.12 \times 0.05$ mm
$\beta = 113.57$ (3)°	

Data collection

Oxford KM-4 CCD area-detector diffractometer	11719 measured reflections
	4234 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2009)	3483 reflections with $I > 2\sigma(I)$
$T_{min} = 0.789$, $T_{max} = 0.956$	$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	191 parameters
$wR(F^2) = 0.057$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 0.88$ e Å^{-3}
4234 reflections	$\Delta\rho_{min} = -0.74$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Re1—N1	2.006 (2)	N2—C2	1.160 (4)
Re1—N2	2.027 (2)	N3—C3	1.169 (3)
Re1—N3	2.006 (2)	S4—O1	1.4545 (18)
S1—C1	1.605 (3)	S4—O2	1.4472 (18)
S2—C2	1.621 (3)	S5—O4	1.4415 (19)
S3—C3	1.603 (3)	S5—O3	1.456 (2)
N1—C1	1.175 (3)		
N1—Re1—N3	88.69 (8)	N3—Re1—N2	89.24 (9)
N1—Re1—N2	91.49 (9)	N1—Re1—N2^i	88.51 (9)

Symmetry code: (i) $-x+1, -y+1, -z$.

Methyl H atoms were initially placed at positions determined on the basis of a local difference Fourier map and then refined as riding

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H2···O2^{ii}	0.91	2.12	2.823 (3)	133
N4—H2···O4^{ii}	0.91	2.60	3.151 (3)	120
N4—H3···O1^{iii}	0.91	2.11	3.010 (3)	172
N4—H4···O1^{iv}	0.91	2.12	2.927 (3)	147

Symmetry codes: (ii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, y - 1, z$; (iv) $-x, -y + 1, -z$.

atoms (C—H = 0.98 Å), with rotational freedom about their respective local C—S bonds, and with U_{iso}(H) = 1.5U_{eq}(C). Ammonium H atoms were found in a difference Fourier map, initially refined using N—H = 0.910 (3) Å and H···H = 1.50 (1) Å restraints, and then refined as riding atoms, with U_{iso}(H) = 1.2U_{eq}(N). The highest peak in the final difference Fourier map was found 0.97 Å from atom Re1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2010) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

References

Bandy, J. A., Truter, M. R. & Vögtle, F. (1981). *Acta Cryst.* B**37**, 1568–1571.
Biagini, P., Calderazzo, F., Marchetti, F., Pampaloni, G., Ramello, S., Salvalaggio, M., Santi, R. & Spera, S. (2004). *Dalton Trans.* pp. 2364–2371.
Brandenburg, K. (2010). *DIAMOND*. Version 3.0. Crystal Impact GbR, Bonn, Germany.
Coles, S. J., Hursthouse, M. B., Beckett, M. A. & Dutton, M. (2003). *Acta Cryst.* E**59**, o1354–o1356.
Cotton, F. A. & Felthouse, T. R. (1981). *Inorg. Chem.* **20**, 2703–2708.
Dikarev, E. V., Becker, R. Y., Block, E., Shan, Z., Haltiwanger, R. C. & Petrukhina, M. A. (2003). *Inorg. Chem.* **42**, 7098–7105.
Dinda, S., Hazra, D. K., Chowdhury, S. R., Helliwell, M., Malik, K. M. A., Mukherjee, M. & Bhattacharyya, R. (2009). *Inorg. Chim. Acta*, **362**, 2108–2116.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Fronczek, F. R. (2006). Private communication.
Fronczek, F. R. (2007). Private communication.
Gonzalez, R., Barboza, N., Chiozzone, R., Kremer, C., Armentano, D., De Munno, G. & Faus, J. (2008). *Inorg. Chim. Acta*, **361**, 2715–2720.
Jana, A. D., Manna, S. Ch., Rosair, G. M., Drew, M. G. B., Mostafa, G. & Chaudhuri, N. R. (2007). *Cryst. Growth Des.* **7**, 1365–1372.
Langs, D. A., Silverton, J. V. & Bright, W. M. (1970). *J. Chem. Soc. D*, pp. 1653–1654.
Małecka, J., Kochel, A. & Mroziński, J. (2002). *Pol. J. Chem.* **76**, 1509–1512.
Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
Sands, D. E. (1963). *Z. Kristallogr.* **119**, 245–251.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Watt, G. & Thompson, R. J. (1963). *Inorg. Synth.* **7**, 190–192.