C6—Fe1—C8	67.8 (1)	C19—Fe2—C20	40.5 (1)
C6—Fe1—C9	67.8 (1)	Fe1—C1—C2	68.6 (1)
C6—Fe1—C10	40.4 (1)	C3—C4—C5	108.1 (2)
C7—Fe1—C8	40.4 (1)	Fe1—C1—C5	68.8 (1)
C7—Fe1—C9	67.9 (1)	Fe1—C1—C23	127.2 (2)
C7—Fe1—C10	68.1 (1)	C2—C1—C5	106.3 (2)
C8—Fe1—C9	40.4 (1)	C2—C1—C23	128.1 (2)
C8—Fe1—C10	68.1 (1)	C5—C1—C23	125.6 (2)
C9—Fe1—C10	40.5 (1)	Fe1—C2—C1	70.4 (2)
C11—Fe2—C12	41.6 (1)	Fe1—C2—C3	69.5 (2)
C11—Fe2—C13	69.6 (1)	C1—C2—C3	108.4 (2)
C11—Fe2—C14	69.6 (1)	Fe1—C3—C2	69.8 (2)
C11—Fe2—C15	41.8 (1)	Fe1—C3—C4	70.0 (2)
C11—Fe2—C16	97.0 (1)	C2—C3—C4	108.3 (2)
C11—Fe2—C17	120.9 (1)	Fe1—C4—C3	69.5 (2)
C11—Fe2—C18	161.5 (1)	Fe1—C4—C5	69.8 (2)
C11—Fe2—C19	147.6 (1)	Fe1—C5—C1	70.4 (2)
Fe1—C5—C4	69.7 (2)	Fe2—C14—C13	70.1 (2)
C1—C5—C4	108.9 (3)	Fe2—C14—C15	68.4 (1)
Fe1—C6—C7	69.9 (2)	C13—C14—C15	108.1 (3)
Fe1—C6—C10	69.9 (2)	Fe2—C15—C11	68.1 (1)
C7—C6—C10	108.5 (2)	Fe2—C15—C14	71.1 (1)
Fe1—C7—C6	69.7 (2)	C11—C15—C14	108.7 (3)
Fe1—C7—C8	69.7 (2)	Fe2—C16—C17	70.4 (2)
C6—C7—C8	107.7 (3)	Fe2—C16—C20	70.2 (2)
Fe1—C8—C7	69.9 (2)	Fe2—C16—C21	122.7 (2)
Fe1—C8—C9	69.9 (2)	C17—C16—C20	106.9 (3)
C7—C8—C9	108.1 (3)	C17—C16—C21	125.8 (3)
Fe1—C9—C8	69.8 (2)	C20—C16—C21	127.3 (3)
C12—C11—C23	126.0 (2)	Fe2—C17—C16	68.4 (1)
C15—C11—C23	127.8 (2)	Fe2—C19—C18	70.6 (2)
Fe2—C12—C11	67.9 (2)	Fe2—C19—C20	69.1 (2)
Fe2—C12—C13	71.1 (2)	C18—C19—C20	108.7 (3)
C11—C12—C13	109.0 (3)	Fe2—C20—C16	68.6 (2)
Fe1—C9—C10	69.8 (2)	Fe2—C20—C19	70.3 (2)
C8—C9—C10	108.2 (3)	C16—C20—C19	108.5 (3)
Fe1—C10—C6	69.8 (2)	Fe2—C17—C18	70.6 (2)
Fe1—C10—C9	69.8 (2)	C16—C17—C18	108.4 (3)
C6—C10—C9	107.5 (3)	Fe2—C18—C17	68.6 (1)
Fe2—C11—C12	70.5 (1)	Fe2—C18—C19	69.4 (2)
Fe2—C11—C15	70.1 (1)	C17—C18—C19	107.5 (3)
Fe2—C11—C23	123.5 (2)	C16—C21—C22	119.2 (2)
C12—C11—C15	106.2 (2)	C21—C22—C23	131.1 (3)
Fe2—C13—C12	68.5 (2)	C1—C23—C11	115.7 (2)
Fe2—C13—C14	69.8 (2)	C1—C23—C22	120.4 (2)
C12—C13—C14	107.9 (3)	C11—C23—C22	123.9 (2)

The *MULTAN*11/82 program system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) was used to solve the structure.

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The 7,7,8,8-Tetracyanoquinodimethane Salt of (C-meso-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II), [Ni(C-meso-Me6[14]aneN4)](TCNQ)2

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Abstract

The title compound, [Ni($C_{16}H_{36}N_4$)]($C_{12}H_4N_4$)$_2$, consists of cationic (C-meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) entities and 7,7,8,8-tetracyanoquinodimethane anions. The Ni atom is surrounded by four N atoms from the tetraaza macrocycle in a square-planar arrangement. The average Ni—N distance is 1.953 (3) Å. The TCNQ$^-$ radical anions are arranged so as to form discrete dimers with the usual twist-type π overlap which leads to a diamagnetic ground state. The intra- and interdimer separations between the mean molecular planes within a TCNQ column are 3.081 (5) and 5.113 (5) Å, respectively.

Comment

7,7,8,8-Tetracyanoquinodimethane (TCNQ) salts have been a classical research subject in the field of low-dimensional molecular conductors (Delhaes, 1992). The combination of the TCNQ⁻ radical anion and cationic transition metal complexes offers the possibility of obtaining new materials with interesting physical properties (both electrical and magnetic) (Lacroix, Kahn, Gleizes, Valade & Cassoux, 1984; Inoue & Inoue, 1986; Bencini, Midollini & Zanchini, 1989; Bencini & Zanchini, 1991; Cornelissen, Van Diemen, Groeneveld, Haasnoot, Spek & Reedijk, 1992; Oshio, Ino, Mogi & Ito, 1993). Here, we report the synthesis and crystal structure of the [Ni(C-meso-Me$_6$[14]-aneN$_4$)](TCNQ)$_2$ salt (I) (Me$_6$[14]aneN$_4$ = 5,5,7,12,12,-14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) which behaves as a poor semiconductor, in accordance with its structure.

(I)
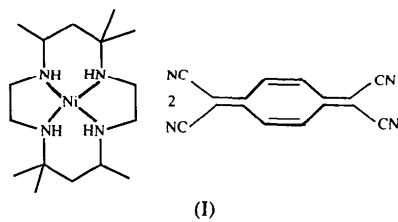
The structure of (I) consists of [Ni(C-meso-Me$_6$[14]-aneN$_4$)]²⁺ cations and TCNQ⁻ anions. A perspective view of both units is shown in Fig. 1 along, with the atom-numbering scheme.
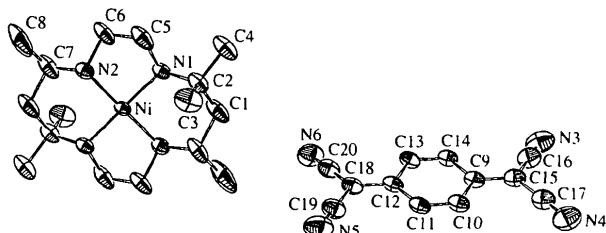

Fig. 1. Labelled perspective view of the [Ni(C-meso-Me$_6$[14]aneN$_4$)] and TCNQ molecules with H atoms omitted for clarity. Displacement ellipsoids are plotted at the 50% probability level.

The Ni atom is surrounded by the four secondary N atoms of the tetraaza macrocycle, yielding a square-planar diamagnetic nickel(II) complex. The values for the Ni—N bond lengths [1.951 (3) and 1.955 (3) Å for Ni—N(1) and Ni—N(2), respectively] lie in the normal range for low-spin nickel(II) complexes with four planar coplanar N donor atoms (Ruiz, Julve, Cano, Soto, Martinez-Mañez, Muñoz & Payá, 1993). The angles subtended at the Ni atom exhibit significant deviations from the ideal value of 90° [86.6 (1) and 93.4 (3)° for N(1)—Ni—N(2) and N(1)—Ni—N(2)(−x, −y, −z), respectively].

The macrocyclic ligand adopts the most stable conformation; the six-membered rings adopt the chair form with atoms C(3) and C(8) in equatorial positions, whereas the five-membered rings are in the gauche conformation. Significant deviations from the tetrahedral angles are observed for angles Ni—N(1)—C(2), Ni—N(2)—C(7) and C(2)—C(1)—C(7)(−x, −y, −z) [120.2 (2), 123.2 (2) and 114.5 (2)°, respectively], these distortions being common to the six-membered chelate rings of the [Ni(C-meso-Me$_6$[14]aneN$_4$)]²⁺ complex where the organic ligand is in a planar conformation (Ruiz, Julve, Cano, Soto, Martinez-Mañez, Muñoz & Payá, 1993).

The bond lengths in the TCNQ⁻ anion are in the usual range for the fully reduced radical species (Hoekstra, Spoelder & Vos, 1972). In fact, a value of −0.87 is obtained when using the usual empirical relation of Kistenmacker (Kistenmacker, Emge, Bloch & Cowan, 1982) to evaluate the formal charge on the radical anion from the average C—C bond distances (1.346 and 1.429 Å for the two endocyclic distances and 1.410 and 1.417 Å for the two exocyclic ones). The TCNQ⁻ anion is almost planar. The C atoms of the aromatic ring do not deviate significantly from planarity. The largest deviations of the outer C atoms from the C(9)–C(14) mean plane are 0.21 and 0.17 Å for atoms C(17) and C(20), respectively.

Two TCNQ⁻ anions related by the (1−x, 1−y, 1−z) symmetry operation form (TCNQ)$_2$²⁻ dimers; the overlapping mode within this dimer is of the usual ring–ring type. The dimers stack to form an infinite chain along the b axis; the intra- and interdimer separation between the mean planes of each quinonoid ring within the chain are 3.081 (5) and 5.113 (5) Å, respectively. The shortest interplanar distance is similar to that found for the analogous [M^{II}(phen)$_3$](TCNQ)$_2$ complexes (M = Zn, Cu; phen = 1,10-phenanthroline) (Bencini, Midollini & Zanchini, 1989), but smaller than that usually observed in TCNQ alkali metal salts (3.22 Å) (Endres, 1983). These columns of TCNQ⁻ anions are separated from one another by the insertion of bulky [Ni(C-meso-Me$_6$[14]-aneN$_4$)]²⁺ complex cations. Considering the structure, no short-range interactions between cations and anions are expected; the Ni···N(5) distance is 6.745 (4) Å and so the Ni atom can be considered to be too distant from the TCNQ 'ligands' to be coordinated, in contrast to the situation in the related [M^{II}(abpt)$_2$](TCNQ)$_2$ complexes [M = Cu, Ni, Co, Fe; abpt = 3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole], where two TCNQ⁻ anions occupy the axial positions in the octahedral environment of the metal ion (Cornelissen, Van Diemen, Groeneveld, Haasnoot, Spek & Reedijk, 1992).

Experimental

Compound (I) was easily synthesized in good yield by metathesis of Li(TCNQ) (211 mg, 1.0 mmol) (Melby, Harder,

Hertler, Mahler, Benson & Mochel, 1962) and [Ni(C-meso-Me₆[14]aneN₄)](ClO₄)₂ (272 mg, 0.5 mmol) (Ruiz, Julve, Cano, Soto, Martinez-Mañez, Muñoz & Payá, 1993) in a 1:1 acetonitrile/methanol solution (50 ml) at room temperature under aerobic conditions. The salt immediately precipitated as a purple crystalline solid, which was filtered off and air dried. Elemental analysis: found, C 63.68, H 5.82, N 22.43%; calculated for $C_{40}H_{44}N_{12}Ni$, C 63.92, H 5.90, N 22.36%. Small purple rhombic crystals of (I) with a metallic lustre, suitable for X-ray data collection, were obtained in more dilute conditions and under an argon atmosphere after one day.

Crystal data
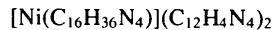
[Ni($C_{16}H_{36}N_4$)]($C_{12}H_4N_4$)₂	Mo $K\alpha$ radiation
$M_r = 751.59$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 8.186(1)$ Å	$\theta = 12–18°$
$b = 11.107(1)$ Å	$\mu = 0.550$ mm^{-1}
$c = 11.515(2)$ Å	$T = 293$ K
$\alpha = 80.28(1)°$	Orthorhombic
$\beta = 76.36(3)°$	$0.4 \times 0.2 \times 0.2$ mm
$\gamma = 68.73(1)°$	Purple
$V = 944.1(3)$ Å³	
$Z = 1$	
$D_x = 1.32$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	2471 observed reflections [$I > 3\sigma(I)$]
$\omega/2\theta$ scans	$R_{int} = 0.025$
Absorption correction:	$\theta_{max} = 25°$
ψ scan (North, Phillips & Mathews, 1968)	$h = 0 \rightarrow 9$
$T_{min} = 0.94$, $T_{max} = 0.98$	$k = -13 \rightarrow 13$
3445 measured reflections	$l = -13 \rightarrow 13$
2501 independent reflections	3 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.1$
$R = 0.042$	$\Delta\rho_{max} = 0.48$ e Å^{-3}
$wR = 0.042$	$\Delta\rho_{min} = -0.62$ e Å^{-3}
$S = 1.7$	Atomic scattering factors
2471 reflections	from *International Tables*
242 parameters	*for X-ray Crystallography*
Riding model for H atoms	(1974, Vol. IV)
Unit weights applied	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0	0	0	0.0249 (3)
N(1)	−0.0032 (3)	0.0174 (3)	−0.1710 (2)	0.0249 (3)
N(2)	0.0725 (4)	0.1537 (3)	−0.0325 (2)	0.0323 (9)
N(3)	0.7031 (5)	0.3219 (4)	0.0812 (4)	0.0762 (10)
N(4)	0.1361 (5)	0.5213 (4)	0.2142 (3)	0.0684 (10)
N(5)	0.9447 (5)	0.7170 (4)	0.5432 (4)	0.0678 (10)
N(6)	0.3732 (5)	0.8955 (4)	0.6802 (4)	0.0756 (10)
C(1)	−0.1343 (5)	−0.1485 (4)	−0.1692 (3)	0.0588 (10)
C(2)	−0.1485 (5)	−0.0071 (3)	−0.2129 (3)	0.0414 (10)
C(3)	−0.3290 (5)	0.0901 (4)	−0.1635 (4)	0.0608 (11)
C(4)	−0.1142 (6)	0.0045 (4)	−0.3504 (3)	0.0540 (10)
C(5)	0.0177 (5)	0.1436 (4)	−0.2253 (3)	0.0540 (10)
C(6)	0.1416 (5)	0.1671 (4)	−0.1637 (3)	0.0510 (10)
C(7)	0.1949 (5)	0.1736 (4)	0.0318 (3)	0.0555 (10)
C(8)	0.2010 (7)	0.3129 (4)	0.0047 (4)	0.1029 (11)
C(9)	0.5056 (4)	0.5348 (3)	0.3079 (3)	0.0323 (10)
C(10)	0.3680 (4)	0.6129 (3)	0.3939 (4)	0.0332 (10)
C(11)	0.4060 (4)	0.6754 (3)	0.4688 (3)	0.0330 (10)
C(12)	0.5835 (4)	0.6671 (3)	0.4684 (3)	0.0326 (10)
C(13)	0.7220 (4)	0.5871 (3)	0.3838 (3)	0.0355 (10)
C(14)	0.6841 (4)	0.5246 (3)	0.3086 (3)	0.0336 (10)
C(15)	0.4615 (4)	0.4724 (3)	0.2290 (3)	0.0389 (10)
C(16)	0.5945 (5)	0.3899 (4)	0.1460 (4)	0.0506 (10)
C(17)	0.2830 (5)	0.4976 (4)	0.2209 (3)	0.0464 (10)
C(18)	0.6226 (4)	0.7344 (3)	0.5457 (3)	0.0390 (10)
C(19)	0.8001 (5)	0.7248 (4)	0.5455 (3)	0.0464 (10)
C(20)	0.4853 (5)	0.8232 (4)	0.6214 (4)	0.0511 (10)

Table 2. *Selected geometric parameters* (Å, °)

Ni—N(1)	1.951 (3)	C(10)—C(11)	1.345 (5)
Ni—N(2)	1.955 (3)	C(11)—C(12)	1.420 (5)
C(2)—N(1)	1.507 (4)	C(12)—C(18)	1.410 (5)
C(5)—N(1)	1.487 (4)	C(16)—C(15)	1.422 (5)
C(4)—C(2)	1.533 (5)	C(19)—C(18)	1.417 (5)
C(8)—C(7)	1.542 (5)	N(4)—C(17)	1.152 (5)
C(6)—N(2)	1.485 (4)	C(20)—N(6)	1.141 (5)
C(7)—N(2)	1.473 (4)	C(9)—C(15)	1.409 (5)
C(5)—C(6)	1.480 (5)	C(10)—C(9)	1.434 (4)
C(1)—C(2)	1.536 (5)	C(12)—C(13)	1.437 (4)
C(3)—C(2)	1.525 (5)	C(14)—C(13)	1.347 (5)
N(3)—C(16)	1.143 (5)	C(17)—C(15)	1.407 (5)
N(5)—C(19)	1.150 (5)	C(20)—C(18)	1.421 (5)
C(14)—C(9)	1.426 (5)		
N(2)—Ni—N(1)	86.6 (1)	C(13)—C(12)—C(18)	121.4 (3)
C(5)—N(1)—C(2)	111.9 (3)	C(12)—C(13)—C(14)	121.3 (3)
C(7)—N(2)—Ni	123.2 (2)	C(17)—C(15)—C(9)	121.6 (3)
C(1)—C(2)—N(1)	106.7 (3)	N(3)—C(16)—C(15)	178.6 (5)
C(4)—C(2)—C(1)	107.3 (3)	C(12)—C(18)—C(20)	121.6 (3)
C(3)—C(2)—C(1)	113.0 (3)	C(19)—C(18)—C(12)	121.8 (3)
C(6)—C(5)—N(1)	107.1 (3)	N(6)—C(20)—C(18)	178.6 (5)
C(2)—N(1)—Ni	120.2 (2)	C(15)—C(9)—C(10)	120.2 (3)
C(6)—N(2)—Ni	106.6 (2)	C(9)—C(10)—C(11)	121.4 (3)
C(5)—C(6)—N(2)	107.6 (3)	C(13)—C(12)—C(11)	116.5 (3)
C(4)—C(2)—N(1)	109.9 (3)	C(18)—C(12)—C(11)	122.1 (3)
C(3)—C(2)—N(1)	109.4 (3)	C(9)—C(14)—C(13)	122.1 (3)
C(3)—C(2)—C(4)	110.6 (3)	C(16)—C(15)—C(17)	116.3 (3)
C(8)—C(7)—N(2)	111.8 (3)	N(4)—C(17)—C(15)	178.4 (4)
C(14)—C(9)—C(10)	116.4 (3)	C(19)—C(18)—C(20)	116.4 (3)
C(15)—C(9)—C(14)	123.4 (3)	N(5)—C(19)—C(18)	178.8 (4)
C(12)—C(11)—C(10)	122.3 (3)		

The structure was solved by Patterson methods and subsequent Fourier maps. All calculations were performed using *SHELXS86* (Sheldrick, 1985) and *SHELX76* (Sheldrick, 1976).

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trans-Hydroxotris(isothiocyanato)bis-(triphenylphosphine)rhenium(IV) Methanol Solvate

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Abstract

The title compound consists of well-separated units of [Re(OH)(NCS)₃(Ph₃P)₂] 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)₃(Ph₃P)₂].MeOH, (1), is formed by the reaction of the well known complex [ReNCl₂(Ph₃P)₂]

(Chatt, Garforth, Johnson & Rowe, 1964) with tri-methylsilylisothiocyanate, Me₃SiNCS. 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 an does an exchange of the chloro ligand occur, but the nitrido ligand is removed and the rhenium is reduced to the Re^IV oxidation state. The air-stable

(1)
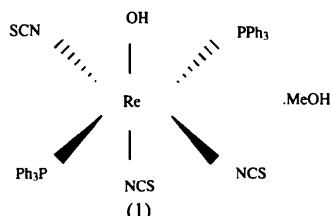
compound is readily soluble in organic solvents such as acetone or CHCl₃. IR studies carried out in solid KBr showed the ν(NCS) stretching vibrations for the isothiocyanate ligands at 1976, 2007 and 2050 cm⁻¹ and the OH absorption band centred at 3379 cm⁻¹. Fast atom bombardment mass spectra of [Re(OH)(NCS)₃(Ph₃P)₂] 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)₃(Ph₃P)₂]⁺, m/z = 843 [ReO(NCS)₂(Ph₃P)₂]⁺, m/z = 827 [Re(NCS)₂(Ph₃P)₂]⁺, m/z = 623 [Re(NCS)₂(Ph₃P)]⁺ and m/z = 565 [Re(NCS)(Ph₃P)]⁺. The nature of the OH⁻ ligand was verified by the recrystallization of the compound from acetone/D₂O, 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⁻¹. The spectroscopic results are confirmed by the structure determination of [Re(OH)(NCS)₃(Ph₃P)₂].MeOH. The title compound consists of discrete monomeric molecules co-crystallized with molecules of solvent methanol in a 1:1 ratio. A *SCHAKAL*89 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⁻ 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-