Charge Transfer Complexes of Nickel Dithiolenes with Methyl Viologen

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Dedicated to Prof. Dr. D. Schulte-Frohlinde on the occasion of his 60th birthday

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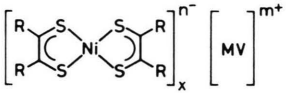
Charge-transfer Complexes, Nickel Dithiolenes, Methyl Viologen, X-Ray

Anionic nickel dithiolenes form crystalline charge-transfer complexes with methyl viologen in its oxidized and reduced forms. X-ray analysis reveals that the planar acceptor methyl viologen interacts with the planar dithiolene donor *via* an expected parallel and a novel perpendicular arrangement.

Introduction

Photoinduced electron transfer is a key step in the conversion of light into chemical energy. In many systems presently investigated, an excited sensitizer in the presence of a reducing agent transfers an electron to methyl viologen (MV^{2+}, 1,1′-dimethyl-4,4′-bipyridinium) [1a]. The reduced MV^{+} is able to reduce carbon dioxide to formic acid [1b] or water to hydrogen in the presence of a catalyst [1a]. In two systems, photoreduction of MV^{2+} was observed in the absence of a sensitizer by irradiating into the charge transfer (CT) bands formed in solutions of MV^{2+} and reducing agents like *p*-phenylenediamine, thiourea [2a] and dithiophosphate [2b]. We recently have found that the same type of photoinduced electron transfer occurs in the CT-complex obtained from a dianionic zinc dithiolene as donor and MV^{2+} as acceptor [3]. This crystalline compound has been the first example of a CT-complex isolated from MV^{2+} and a metal dithiolene. In the following we report on the syntheses and solid state structures of CT-complexes between MV^{2+} or MV^{+} and nickel dithiolenes (Fig. 1). The only other structurally characterized CT-complexes of MV^{2+} have halogenometallates and tetracyanonickelate(II) as counter ions [4]. While some CT-complexes of dithiolenes with organic acceptors [5a] and donors [5b, c] have been reported, the molecular structures are known only for complexes of nickel or platinum dithiolenes with the radical monocations of tetrathiafulvalene [5b], perylene [5c], tetramethyl-*p*-phenylenediamine (TMPD) [5d, e], cycloheptatriene [5f], 4-methoxycarbonyl-1-ethylpyridinium (Rpy^{+}) [5g], phenazine [5h], phenothiazine [5h], and N-methylphenazine [5i].



	n	m	x	R
1	2	2	1	CN
2	1	2	2	Ph
3	1	1	1	Ph

Fig. 1. Isolated complexes **1–3.**

Results

Compounds **1, 2** or **3** are prepared in yields of 80–90% by adding the dissolved sodium salts of the corresponding nickel dithiolenes [6a, b] to a solution of MV^{2+} or MV^{+}, respectively. They are soluble in polar solvents like dimethyl sulfoxide (DMSO) and dimethyl formamide. The presence if MV^{+} in **3** is demonstrated by the characteristic absorption band [7] at $\lambda_{max} = 660$ nm (DMSO) which disappears upon bubbling the solution of **3** with air.

The structure of **1** consists of columns of alternating planar donors and acceptors if viewed along the *a*-axis. These are arranged approximately parallel (dihedral angle of 5.4°) in such a way that one half of MV^{2+} (N(54′)-part) is in close contact with one half (Ni–S(1)–C(1)–C(2)–S(2)) of the nickel dithiolene while the second half is closer to the next dithiolene neighbour. The shortest distance (d) be-

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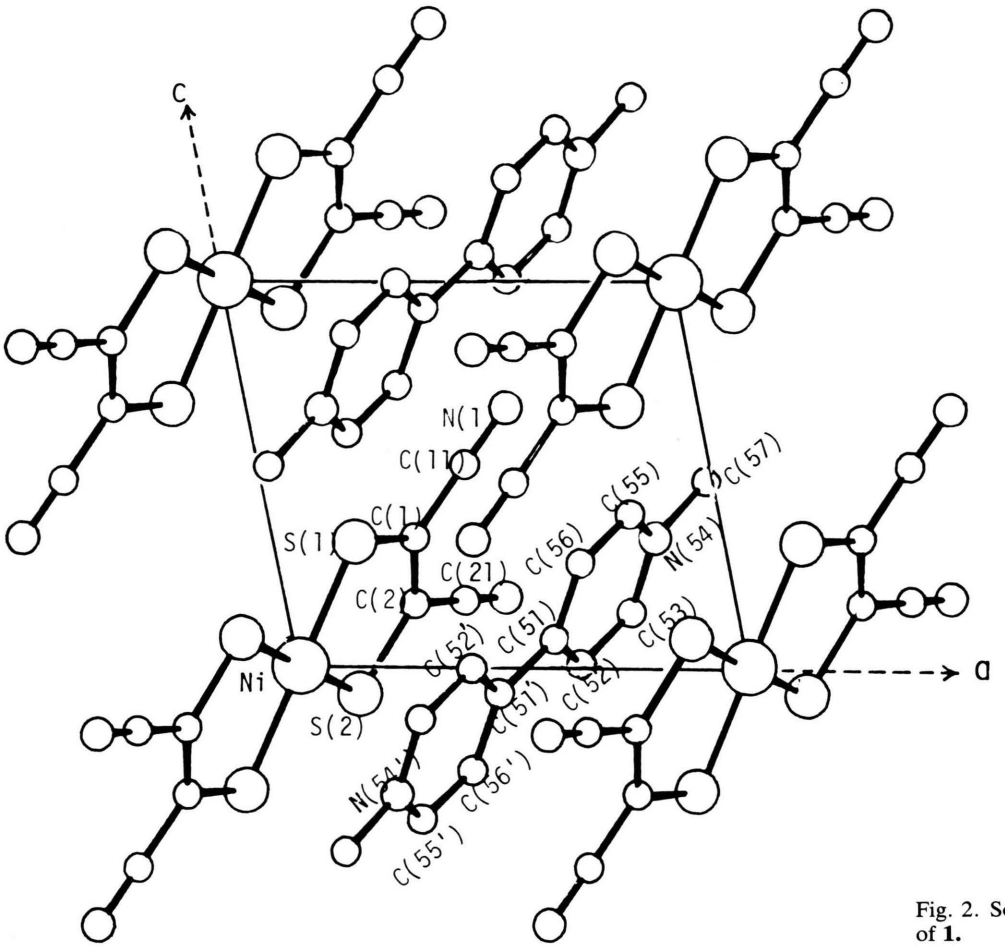

Fig. 2. Solid state structure of **1.**

tween these planes is 3.4 Å and thus indicates a non-localised CT-interaction as observed in the classical organic CT-complexes like hexamethylbenzene-chloranil (d = 3.5 Å) [8]. In the reflectance spectrum of **1** a broad band appears at 530–660 nm. It is absent in the separated donor and acceptor molecules and is therefore assigned to a CT-transition.

The characteristic bond lengths within the nickel dithiolene, Ni–S = 2.18, C–S = 1.73 and C–C = 1.37 Å, compare well with the analogous complexes having $[Rpy^+]_2$ and $[TMPD^+]_2$ as cations. In the two latter cases the dihedral angles between the donor and acceptor planes are 10.8 [4g] and 59° [5d], respectively.

The structure of **2** contains, similar to **1,** an alternating chain of planar ions along the *a*-axis. Now, the dihedral angle between these planes is 21.9° and the shortest distance, S(1)–N(54′), is 3.48 Å. Surprisingly, the second dithiolene is located almost perpendicular (82.9°) to the MV^{2+}-plane, which has an eclipsed orientation relative to the linear S(3′)–Ni(2)–S(3) group. This leads to short contacts of 3.55 and 3.61 Å between the aromatic carbons C(55), C(56) and the sulfur atom S(3), respectively. The calculated distances for S(3)–H(C55) and S(3)–H(C56) are 2.76 and 3.00 Å, respectively. From this arrangement a localised coulombic interaction between MV^{2+} and the second nickel dithiolene is inferred to occur *via* S(3). The known nucleophilic character [6b] of the dithiolene sulfur atoms supports this interpretation. The bond lengths within both dithiolene anions agree with the literature values of

Table I. Crystal data of **1** and **2**.

Compound	**1**	**2**
Formula	$C_{20}H_{14}N_6NiS_4$	$C_{68}H_{54}N_2Ni_2S_8$
Weight	525.3	1273.1
Crystal size/mm	0.4×0.5×0.2	0.45×0.25×0.15
Space group (crystal system)	$P\bar{1}$ (triclinic)	$P\bar{1}$ (triclinic)
a [Å]	7.691(4)	13.670(8)
b [Å]	11.193(3)	13.736(4)
c [Å]	6.432(3)	9.760(3)
α [°]	97.14(2)	105.79(3)
β [°]	96.98(4)	94.42(4)
γ [°]	90.28(3)	118.56(3)
U [Å^3]	545.3	1501.6
Z	1	1
D_m (floating)/g cm^{-3}	1.58	1.40
D_c/g cm^{-3}	1.60	1.41
F (000)	268	660
Radiation (λ)/Å	Mo–K_α(0.7107)	Mo–K_α(0.7107)
μ/cm^{-1}	12.2	9.0
No. of unique reflections	1257	3700
$[(\sin\theta)/\lambda]_{max}$	0.65	0.65
R	0.047	0.041
R'	0.052	0.042
Residual electron density (e Å^{-3})	0.50	0.32

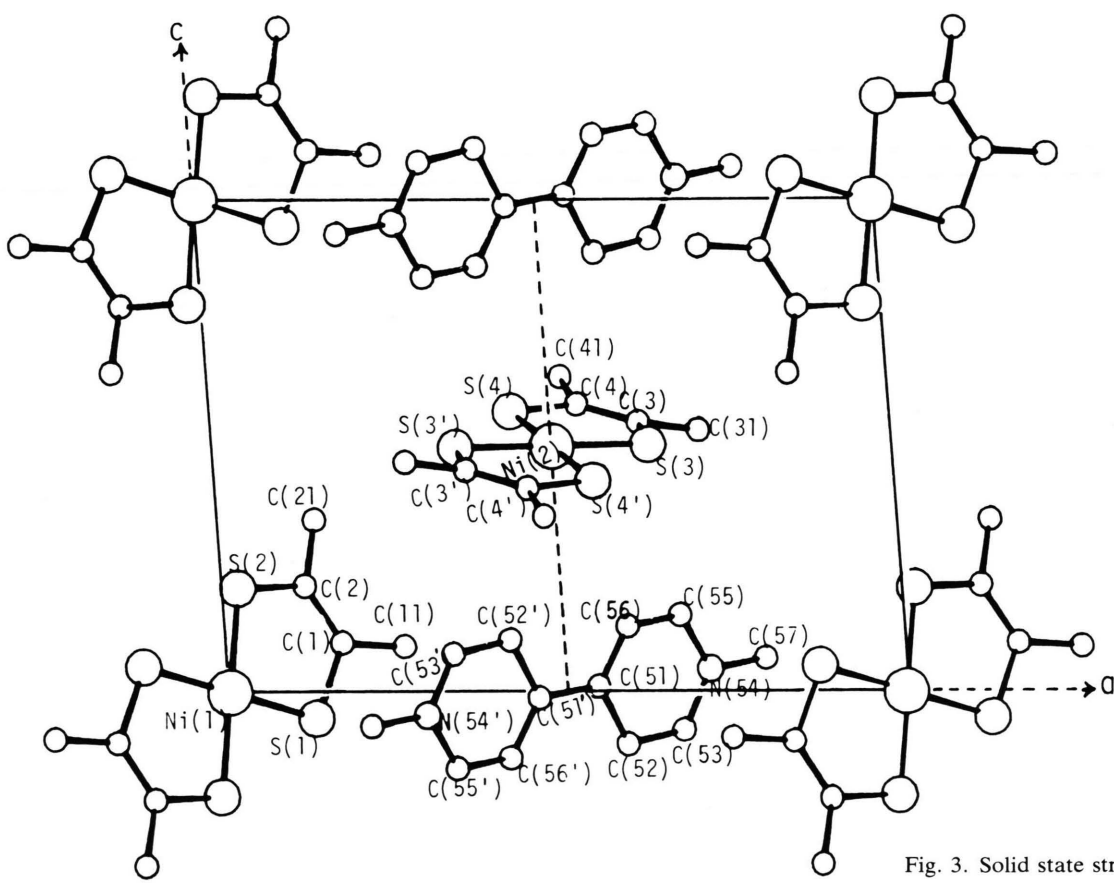

Fig. 3. Solid state structure of **2**.

an analogous complex having tetraethylammonium as the counterion [6c], expect the short Ni(2)–S(3) distance of 2.128(2) Å which may be a result of the S(3)–C(55,56) interaction.

In summary, the structures of the two new complexes **1** and **2** demonstrate two different interactions of the planar acceptor MV^{2+}. A non-localised and a localised interaction which are distinguishable by approximately parallel and perpendicular orientations relative to the planar ditiolene donor, respectively. Perpendicular arrangements are a rare phenomenon and have been observed recently in intramolecular CT-complexes of rigid, tricyclic organic compounds [9].

Table II. Selected bond distances (Å) and angles (°) within **1** and **2.**

Compound	**1**	**2**
(a) Bond lengths		
Ni(1)–S(1)	2.167(2)	2.146(2)
Ni(1)–S(2)	2.181(2)	2.145(1)
Ni(2)–S(3)		2.128(2)
Ni(2)–S(4)		2.144(2)
S(1)–C(1)	1.734(7)	1.745(4)
S(2)–C(2)	1.738(6)	1.735(4)
S(3)–C(3)		1.738(5)
S(4)–C(4)		1.740(4)
C(1)–C(2)	1.372(9)	1.365(6)
C(3)–C(4)		1.380(9)
C(1)–C(11)	1.430(9)	1.492(6)
C(2)–C(21)	1.427(10)	1.496(5)
C(3)–C(31)		1.483(7)
C(4)–C(41)		1.479(6)
C(11)–N(1)	1.131(8)	
C(21)–N(2)	1.129(10)	
C(51)–C(52)	1.375(10)	1.488(16)
C(51)–C(56)	1.379(9)	1.320(18)
C(52)–C(53)	1.383(9)	1.381(19)
C(53)–N(54)	1.336(9)	1.339(14)
N(54)–C(55)	1.337(10)	1.446(15)
C(55)–C(56)	1.361(10)	1.415(18)
N(54)–C(57)	1.494(9)	1.466(16)
C(51)–C(51′)	1.492(8)	1.472(18)
(b) Angles		
S(1)–Ni(1)–S(2)	92.1(1)	90.6(1)
S(3)–Ni(2)–S(4)		91.0(1)
Ni(1)–S(1)–C(1)	103.6(2)	105.8(2)
Ni(1)–S(2)–C(2)	103.4(2)	105.7(2)
Ni(2)–S(3)–C(3)		105.9(2)
Ni(2)–S(4)–C(4)		105.8(2)
S(1)–C(1)–C(2)	120.7(5)	118.5(3)
S(2)–C(2)–C(1)	120.1(5)	119.3(3)
S(3)–C(3)–C(4)		118.9(3)
S(4)–C(4)–C(3)		118.3(3)
C(52)–C(51)–C(56)	117.0(6)	118.9(12)
C(51)–C(52)–C(53)	120.9(6)	116.1(10)
C(52)–C(53)–N(54)	120.4(7)	127.6(10)
C(53)–N(54)–C(55)	119.3(6)	112.9(9)
N(54)–C(55)–C(56)	121.9(7)	122.9(10)
C(55)–C(56)–C(51)	120.4(7)	120.4(11)

Experimental Part

Nickel dithiolenes were prepared acc. to ref. [6a,b]. $MVCl_2 \cdot 3H_2O$ was a commercial product (Wako-Chemicals). All manipulations with **2** and **3** were performed under an argon atmosphere.

(1,1′-Dimethyl-4,4′-bipyridinium)-bis(cis-1,2-dicyano-1,2-ethylenedithiolate)niccolate (2^-) (**1**)

To a filtered solution of 380 mg (2 mmol) of disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate are added 260 mg (1 mmol) of $Ni(OAc)_2 \cdot 4H_2O$ dissolved in 8 ml of H_2O/DMSO = 1/1. After 5 min a solution of 1 g (3.2 mmol) of $MVCl_2 \cdot 3H_2O$ is added. The brown precipitate formed immediately is filtered off after standing over night and washed with MeOH and THF, respectively; 292 mg (55%). Recrystallisation from DMSO/MeOH yields brown crystals of **1,** Fp(dec.) > 320 °C.

Analysis for $C_{20}H_{14}N_6S_4Ni$

Calcd C45.73 H2.69 N16.00 S24.41 Ni11.18,
Found C45.57 H2.89 N15.88 S24.78 Ni11.33.

(1,1′-Dimethyl-4,4′-bipyridinium)-bis[bis(cis-1,2-diphenyl-1,2-ethylenedithiolate)niccolate](2^-)(**2**)

To a suspension of 0,25 g (0,46 mmol) of bis(*cis*-1,2-diphenyl-1,2-ethylenedithiolate)nickel in 18 ml of THF/DMSO = 2/1 are added 0,038 g (1 mmol) of $NaBH_4$ in 10 ml of THF/MeOH = 1/1. After 20 min the deep red solution is filtered under Ar into 0.5 g (1.6 mmol) of $MVCl_2 \cdot 3H_2O$ dissolved in 15 ml of H_2O/MeOH = 1/4. After standing over night at 4 °C, the crystals are filtered off and washed with MeOH; 0.26 g (89%). Recrystallisation from DMSO/MeOH yields black crystals of **2,** Fp(dec.) > 320 °C.

Analysis for $C_{68}H_{54}N_2Ni_2S_8$

Calcd C64.18 H4.25 N2.20 Ni9.2 S20.13,
Found C63.85 H4.36 N2.28 Ni9.04 S18.04.

(1,1′-Dimethyl-4,4′-bipyridinium)-bis(cis-1,2-diphenyl-1,2-ethylenedithiolate)niccolate(1^-) (**3**)

To a suspension of 0.3 g (0.5 mmol) of bis(*cis*-1,2-diphenyl-1,2-ethylenedithiolate)nickel in 30 ml of DMSO/MeOH = 1/2 are added 0.1 g (2.6 mmol) of $NaBH_4$. After 10 min of vigorous stirring, 2 ml of acetone are added. This deep red solution is filtred under Ar into MVCl (prepared from 0.47 g

Table III. Atomic coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^3$) in the form of $\mathrm{Exp}(-(\mathrm{B}11\times h^2+2\mathrm{B}12\times h\times k+\cdots)$.

Atom	*x*	*y*	*z*	B11	B22	B33	B12	B13	B23
(a) Complex **1**									
Ni	0(0)	0(0)	0(0)	14(0)	5(0)	18(0)	−1(0)	1(0)	2(0)
S(1)	1379(2)	659(2)	3072(3)	21(0)	6(0)	20(0)	−3(0)	−3(0)	3(0)
S(2)	246(2)	1744(1)	1129(3)	21(0)	6(0)	19(0)	−2(0)	−2(0)	3(0)
C(1)	1928(8)	2136(6)	2839(10)	14(1)	6(2)	22(2)	−1(1)	2(1)	3(1)
C(2)	1394(8)	2625(6)	1021(10)	15(1)	6(1)	19(2)	−1(1)	1(1)	2(1)
C(11)	2971(9)	2819(6)	4579(10)	16(1)	7(1)	22(2)	0(1)	2(1)	2(1)
C(21)	1855(9)	3840(6)	828(11)	19(2)	8(1)	22(2)	2(1)	1(1)	2(1)
N(1)	3854(9)	3314(6)	5955(10)	25(2)	9(1)	27(2)	−3(1)	−5(1)	2(1)
N(2)	2251(11)	4797(6)	693(11)	38(2)	9(1)	34(2)	−6(1)	1(2)	4(1)
C(51)	5426(8)	567(5)	572(10)	11(1)	7(1)	21(2)	1(1)	5(1)	3(1)
C(52)	5361(10)	1626(6)	311(11)	20(2)	7(1)	24(2)	0(1)	0(1)	4(1)
C(53)	6150(10)	2670(6)	781(12)	21(2)	8(17	29(2)	1(1)	4(2)	6(1)
N(54)	6993(7)	2667(5)	2723(9)	17(1)	7(1)	26(2)	1(1)	5(1)	1(1)
C(55)	7096(10)	1639(7)	3587(11)	18(2)	9(1)	26(2)	0(1)	−3(1)	1(1)
C(56)	6339(10)	594(6)	2560(11)	19(2)	8(1)	27(2)	0(1)	−1(1)	5(1)
C(57)	7788(12)	3802(7)	3947(14)	28(2)	7(1)	40(3)	4(1)	6(2)	−3(1)
(b) Complex **2**									
Ni(1)	0(0)	0(0)	0(0)	6(0)	7(0)	7(0)	3(0)	1(0)	1(0)
Ni(2)	5000(0)	0(0)	5000(0)	6(0)	7(0)	10(0)	4(0)	1(0)	3(0)
S(1)	1735(1)	859(1)	−220(0)	6(0)	8(0)	6(0)	3(0)	1(0)	1(0)
S(2)	603(1)	660(1)	2344(1)	6(0)	10(0)	7(0)	3(0)	1(0)	2(0)
S(3)	6771(1)	573(1)	5235(1)	7(0)	8(0)	14(0)	5(0)	2(0)	1(0)
S(4)	5426(1)	1740(1)	6326(1)	6(0)	8(0)	12(0)	4(0)	2(0)	2(0)
C(1)	2604(3)	1575(4)	1566(4)	6(0)	6(0)	7(0)	3(0)	1(0)	1(0)
C(2)	2088(4)	1529(4)	2709(4)	7(0)	6(0)	6(0)	4(0)	1(0)	1(0)
C(3)	7521(4)	2085(4)	6230(5)	6(0)	8(0)	11(1)	4(0)	1(0)	2(0)
C(4)	6918(4)	2606(4)	6781(5)	6(0)	8(0)	10(1)	4(0)	1(0)	3(0)
C(11)	3868(4)	2177(4)	1703(4)	6(0)	6(0)	8(0)	3(0)	2(0)	1(0)
C(12)	4599(4)	2174(4)	2781(5)	7(0)	9(0)	9(1)	5(0)	2(0)	3(0)
C(13)	5764(4)	2721(5)	2891(5)	8(0)	11(1)	13(1)	6(0)	1(0)	2(1)
C(14)	6229(4)	3254(5)	1896(6)	6(0)	9(1)	16(1)	3(0)	3(0)	0(1)
C(15)	5521(4)	3244(5)	789(6)	8(0)	10(1)	13(1)	4(0)	4(0)	4(1)
C(16)	4348(4)	2709(4)	700(5)	7(0)	9(0)	9(1)	3(0)	2(0)	2(0)
C(21)	2693(3)	2222(4)	4296(4)	5(0)	7(0)	7(0)	4(0)	1(0)	1(0)
C(22)	2465(4)	1667(4)	5333(4)	7(0)	8(0)	8(0)	4(0)	1(0)	2(0)
C(23)	3010(4)	2333(5)	6808(5)	9(0)	10(1)	9(1)	5(0)	1(0)	4(0)
C(24)	3759(4)	3530(5)	7258(5)	8(0)	12(1)	8(1)	5(0)	0(0)	1(0)
C(25)	3985(4)	4096(4)	6248(5)	7(0)	8(0)	11(1)	3(0)	1(0)	0(0)
C(26)	3444(4)	3440(4)	4764(5)	7(0)	7(0)	9(1)	3(0)	1(0)	2(0)
C(31)	8766(4)	2713(5)	6292(5)	6(0)	10(1)	13(1)	4(0)	−2(1)	0(1)
C(32)	9362(5)	2120(6)	6356(7)	8(1)	12(1)	26(1)	7(1)	−3(1)	− 5(1)
C(33)	10505(6)	2657(8)	6242(9)	9(1)	23(1)	34(2)	11(1)	5(1)	−12(1)
C(34)	11020(6)	3731(9)	6075(9)	8(1)	30(1)	27(1)	8(1)	6(1)	− 4(1)
C(35)	10471(5)	4335(7)	6063(8)	8(1)	21(1)	23(1)	3(1)	4(0)	6(1)
C(36)	9332(4)	3819(6)	6159(6)	7(0)	15(1)	17(1)	4(0)	2(0)	5(1)
C(41)	7414(4)	3838(4)	7790(5)	7(0)	7(0)	11(1)	4(0)	0(0)	2(0)
C(42)	8278(4)	4322(4)	9053(5)	8(0)	8(0)	13(1)	5(0)	−2(1)	2(0)
C(43)	8684(5)	5442(5)	10034(6)	10(1)	10(1)	17(1)	5(0)	2(1)	0(1)
C(44)	8231(6)	6111(6)	9810(7)	15(1)	9(1)	21(1)	8(1)	2(1)	− 2(1)
C(45)	7383(6)	5646(6)	8567(8)	16(1)	10(1)	24(1)	9(1)	0(1)	1(1)
C(46)	6965(5)	4523(5)	7569(6)	10(1)	10(1)	17(1)	6(0)	17(2)	3(1)
C(51)	5631(11)	309(11)	10229(11)	62(4)	20(2)	13(2)	31(3)	13(1)	9(1)
C(52)	6318(11)	842(8)	9241(8)	53(2)	15(1)	15(1)	17(1)	7(2)	7(1)
C(53)	7496(11)	1409(8)	9730(10)	49(2)	17(1)	23(2)	20(1)	14(1)	7(1)
N(54)	8098(8)	1679(6)	11064(8)	47(2)	20(1)	31(1)	26(1)	27(2)	10(1)
C(55)	7383(12)	1109(10)	11954(10)	53(2)	32(2)	30(2)	34(2)	26(2)	21(2)
C(56)	6171(12)	397(10)	11479(10)	57(2)	40(2)	31(2)	41(2)	14(2)	25(2)
C(57)	9355(11)	2402(10)	11549(12)	39(2)	24(2)	44(3)	23(2)		13(2)

(1.96 mmol) of $Na_2S \cdot 9H_2O$ and 0.311 g (1 mmol) of $MVCl_2 \cdot 3H_2O$) dissolved in 30 ml of MeOH/H_2O = 1/1. The pink powder produced is filtered off after 2 h and washed with MeOH; 0,348 g (95%). Recrystallisation from DMSO/MeOH gives blue-black crystals of **3,** Fp(dec.) > 320 °C.

Analysis for $C_{40}H_{34}N_2NiS_4 \cdot (CH_3)_2SO$

Calcd	C 62.47	H 4.95	N 3.47,
Found	C 62.80	H 4.68	N 3.68.

X-ray analyses

Suitable crystals for X-ray analyses were obtained by crystallisation from DMS/MeOH. See ref. [10] for experimental details.

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