Crystal Structure of μ^{I}, μ^{II}, μ^{III}-Tris(dithioacetato)-μ_3-trithio-orthoacetato-*triangulo*-trinickel(II) in Two Crystalline Forms

By **Mario Bonamico,* Giulia Dessy, Vincenzo Fares,** and **Lucio Scaramuzza,** Laboratorio di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Co-ordinazione del C. N. R., Via Montorio Romano, 36 00131 Roma, Italy

The title compound crystallizes in two orthorhombic forms: form (I) with a = 8.999(5), b = 14.311(5), c = 14.116(5) Å, and form (II) with a = 7.562(10), b = 17.283(10), c = 14.130(10) Å, both in space group $Pna2_1$. The complex units in the two structures are similar, and consist of a trigonal pyramid-like molecule, which is an example of a transition-metal cluster. The structures were solved from X-ray data by the heavy-atom technique and refined by least squares to R 0.063 (I) and 0.077 (II) for 1 041 and 1 076, respectively, visually estimated independent reflections. Three nickel atoms (forming a regular triangle with presumably non-bonded Ni • • • Ni 3.0 Å), and two different kinds of ligands [three molecules of the dithioacetate ligand and one of the sulphur-substituted ortho-form of acetic acid ($\mathrm{MeCS_3^{3-}}$)] are present. The co-ordination of the nickel atoms is essentially square planar: two have short distances (3.2 Å) to sulphur atoms of neighbouring molecules, to give a one-dimensional polymeric system.

As part of an investigation of variation in structure of transition-metal complexes with sulphur-containing bidentate ligands, we intended to examine the crystal structure of bis(dithioacetato)nickel(II). However, attemps to obtain crystals of this complex led to a new compound, with a much higher molecular weight, as described by Furlani *et al.*[1] This new complex was obtained in two different forms, (I) and (II), and we have carried out an X-ray analysis of both forms in order to identify the molecular structure and to ascertain possible structural differences between them.

EXPERIMENTAL

Preparation.—Form (I) was obtained by treatment of bis(dithioacetato)nickel with carbon disulphide–ethanol. Presumably the latter is responsible for the transformation $[-\mathrm{C}(\dot{:}\mathrm{S})\mathrm{S}^-]\rightarrow[-\mathrm{C}(\mathrm{S}^-)_3]$, and for formation of the trinuclear complex. Form (II) was obtained by reaction of 2 : 1 molar proportions of (dithioacetato)sodium and $\mathrm{NiCl_2}$ in water.[1] Crystals of both forms are shiny black orthorhombic prisms, stable in air and to X-rays.

Crystal Data and Intensity Measurements.—Crystal data for each form are summarized in Table 1. Unit cell dimensions were determined, by an improved version of Christ's method,[2] from zero-layer Weissenberg film taken about the a and b [form(I)] and about the b and c axes [form (II)]. The space group was determined from systematic absences and confirmed by the subsequent successful structure determination. Densities were measured by flotation.

TABLE 1

Formula		$\mathrm{C_8H_{12}Ni_3S_9}$	
M	Form (I)	572.85	Form (II)
Space group	$Pna2_1$		$Pna2_1$
a/Å	8.999(5)		7.562(10)
b/Å	14.311(5)		17.283(10)
c/Å	14.116(5)		14.130(10)
U/Å^3	1 847		
Z	4		4
D_c/g cm^{-3}	2 093		2.061
D_m/g cm^{-3}	2.06(2)		2.02(2)
μ(Cu-K_α)/cm^{-1}	125.0 cm^{-1}		123.2
F(000)		1 102.44	
No. of reflections	1 041		1 076
Layers	0—7kl		hk0—8 h0—10l

Intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs. Absorption or extinction were not allowed for, but corrections for the Lorentz and polarisation effects and for spot extensions[3] were applied. Initial scaling was based on the relative exposure times of the different photographs. Independent layer scales were refined during the isotropic phase of the structure refinement.

Determination and Refinement of the Structures.—Both structures were solved by the usual combination of Patterson and Fourier methods. Non-hydrogen atomic positional and isotropic thermal parameters were refined by several cycles of 4 × 4 block-diagonal least-squares, the function minimised being $\Sigma w(|F_o| - k|F_c|)^2$. At the end of isotropic refinement R values were 0.093 [form (I)] and 0.145 [form (II)]. The refinements were continued by use of anisotropic thermal parameters, until convergence was achieved (final shifts in atomic parameters $<0.2\sigma$). The final R values were 0.063 (I) and 0.077 (II) for the two forms. The weighting scheme $w = (a + bF_o + cF_o^2)^{-1}$ was used throughout the refinements with $a = 4.0$, $b = 1.0$, and $c = 0.005$ for

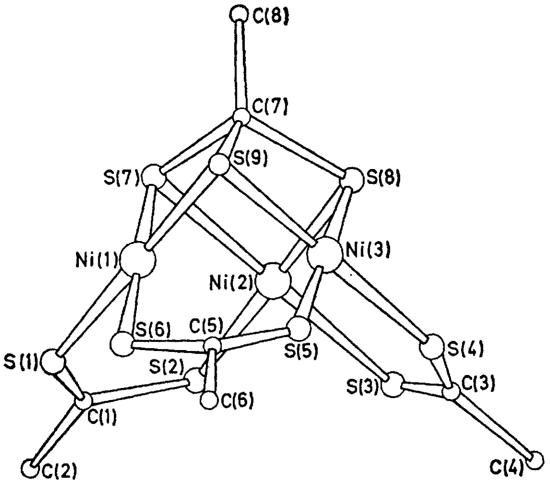

FIGURE 1

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[1] C. Furlani, A. Flamini, A. Sgamellotti, and C. Bellitto, *J.C.S. Dalton*, 1973, 2404.

[2] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca Sci.*, 1963, **33**, (II*A*), 1113.

[3] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

both structures. Table 2 gives final atomic parameters and their standard deviations, within the crystal-chemical units, for both forms.

Bond distances and angles within the crystal-chemical units are shown, with their estimated standard deviations, in Table 3.

TABLE 2

Positional (× 10^4) and thermal parameters,* with estimated standard deviations in parentheses

(*a*) Form (I)

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Ni(1)	2 813(3)	188(2)	1 057(7)	100(5)	5(4)	−26(11)	30(1)	−7(7)	51(2)
Ni(2)	73(5)	−188(4)	2 114(3)	68(9)	7(7)	7(7)	33(3)	23(5)	35(3)
Ni(3)	−3(7)	−158(4)	0(5)	151(12)	−9(9)	14(10)	32(3)	16(5)	56(4)
S(1)	4 161(9)	−538(7)	2 112(9)	90(13)	−1(12)	−30(15)	44(5)	15(9)	59(6)
S(2)	1 297(11)	−963(6)	3 186(8)	136(16)	−20(15)	−31(15)	44(5)	56(8)	60(6)
S(3)	−1 612(11)	−1 292(7)	2 112(8)	168(16)	27(13)	−59(15)	46(6)	−10(8)	58(5)
S(4)	−1 678(10)	−1 276(6)	−43(8)	110(12)	−84(12)	−45(13)	40(5)	−34(8)	62(6)
S(5)	1 274(12)	−927(6)	−1 104(8)	150(15)	34(15)	−7(14)	51(6)	13(7)	39(4)
S(6)	4 099(12)	−534(9)	−43(10)	166(19)	79(19)	14(19)	70(8)	−10(11)	75(9)
S(7)	1 504(11)	1 022(7)	2 078(8)	130(15)	29(12)	22(15)	39(5)	−38(8)	58(6)
S(8)	−1 124(5)	672(3)	1 071(11)	101(7)	15(6)	−11(19)	34(2)	15(11)	54(2)
S(9)	1 576(9)	1 045(5)	71(7)	117(13)	−29(9)	15(12)	22(3)	−16(6)	44(5)
C(1)	3 081(43)	−1 015(24)	3 095(31)	171(63)	−169(52)	−75(68)	54(19)	3(37)	110(31)
C(2)	4 111(47)	−1 393(21)	3 857(32)	231(63)	−27(37)	−120(65)	12(10)	34(27)	101(29)
C(3)	−2 182(22)	−1 637(12)	1 167(38)	120(29)	22(23)	100(45)	27(7)	14(22)	61(14)
C(4)	−3 369(22)	−2 400(13)	1 192(24)	92(30)	−63(24)	−29(35)	44(9)	−8(20)	36(20)
C(5)	3 170(25)	−936(14)	−891(15)	133(46)	115(32)	20(32)	26(11)	−2(16)	22(10)
C(6)	3 947(41)	−1 588(23)	−1 609(22)	191(54)	7(51)	111(44)	54(20)	−26(27)	32(13)
C(7)	416(25)	1 484(10)	1 053(32)	208(39)	−6(29)	−132(66)	24(7)	−2(40)	56(11)
C(8)	10(28)	2 511(13)	1 138(34)	254(46)	97(32)	−112(72)	29(7)	−21(43)	56(18)

(*b*) Form (II)

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Ni(1)	213(4)	1 461(1)	1 076(7)	333(7)	−8(4)	−5(20)	33(1)	−10(7)	81(2)
Ni(2)	195(11)	−36(4)	0(5)	393(6)	−28(9)	7(16)	40(2)	6(6)	58(3)
Ni(3)	186(7)	−46(4)	2 074(3)	225(9)	20(6)	12(15)	36(2)	−9(5)	74(4)
S(1)	1 908(19)	1 989(7)	−28(10)	479(35)	−51(20)	11(25)	47(4)	15(9)	73(6)
S(2)	1 990(18)	458(6)	−1 071(10)	474(32)	−24(18)	34(27)	46(4)	10(8)	54(5)
S(3)	1 741(18)	−1 123(5)	−57(9)	477(30)	102(15)	13(22)	39(3)	5(8)	68(5)
S(4)	1 784(14)	−1 095(6)	2 084(9)	330(20)	21(13)	−53(23)	53(4)	−3(9)	76(6)
S(5)	1 961(16)	466(7)	3 136(11)	300(22)	−50(15)	−14(24)	53(5)	−8(9)	91(8)
S(6)	1 830(18)	2 024(6)	2 155(11)	487(34)	−85(17)	1(30)	37(3)	−10(9)	103(9)
S(7)	−1 601(16)	940(6)	13(9)	389(28)	54(16)	−102(27)	41(3)	−13(10)	109(8)
S(8)	−1 702(6)	−477(3)	1 064(13)	291(9)	−22(6)	−27(27)	39(1)	−16(9)	78(3)
S(9)	−1 625(12)	944(6)	1 997(8)	280(18)	5(12)	29(23)	47(3)	−29(9)	88(7)
C(1)	2 438(48)	1 396(18)	−935(28)	303(77)	66(45)	−127(82)	39(11)	−40(32)	147(36)
C(2)	3 753(85)	1 649(21)	−1 703(35)	630(141)	−66(70)	178(103)	45(13)	46(30)	93(27)
C(3)	2 306(23)	−1 454(12)	1 063(34)	232(34)	32(29)	17(90)	53(8)	131(35)	138(23)
C(4)	3 468(33)	−2 189(11)	851(16)	439(59)	84(32)	−15(44)	42(6)	32(17)	38(18)
C(5)	2 385(58)	1 446(19)	2 977(17)	621(126)	−227(73)	−28(63)	68(16)	−44(24)	17(10)
C(6)	3 547(77)	1 851(22)	3 750(33)	515(111)	−26(62)	−88(88)	47(13)	−11(26)	76(24)
C(7)	−2 857(31)	477(13)	1 110(41)	361(49)	−43(34)	−94(110)	52(8)	33(40)	84(19)
C(8)	−4 692(34)	432(18)	1 245(43)	274(49)	1(44)	94(80)	88(13)	−75(49)	149(51)

* The exponential coefficients b_{ij} given are defined by : $T = \exp[-10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

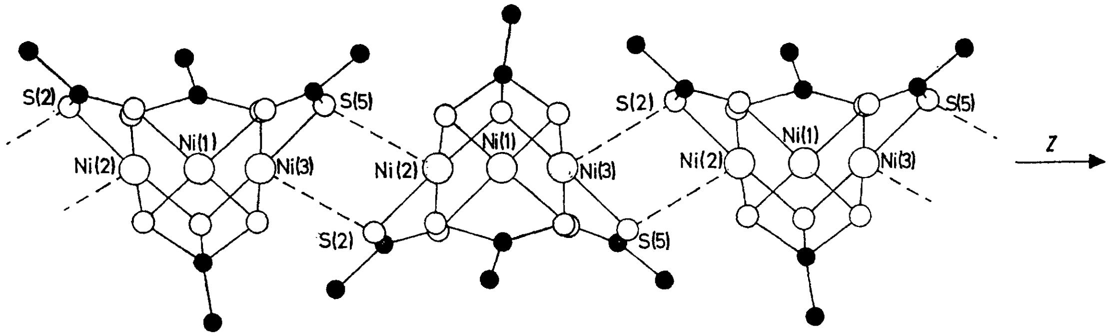

FIGURE 2

Structure factors, based on the final atomic parameters, compared with the observed structure amplitudes, are listed in Supplementary Publication No. SUP 21484 (13 pp., 1 microfiche).*

Calculations.—Calculations were carried out on a Univac 1108 computer at Rome University, by use of the system of

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

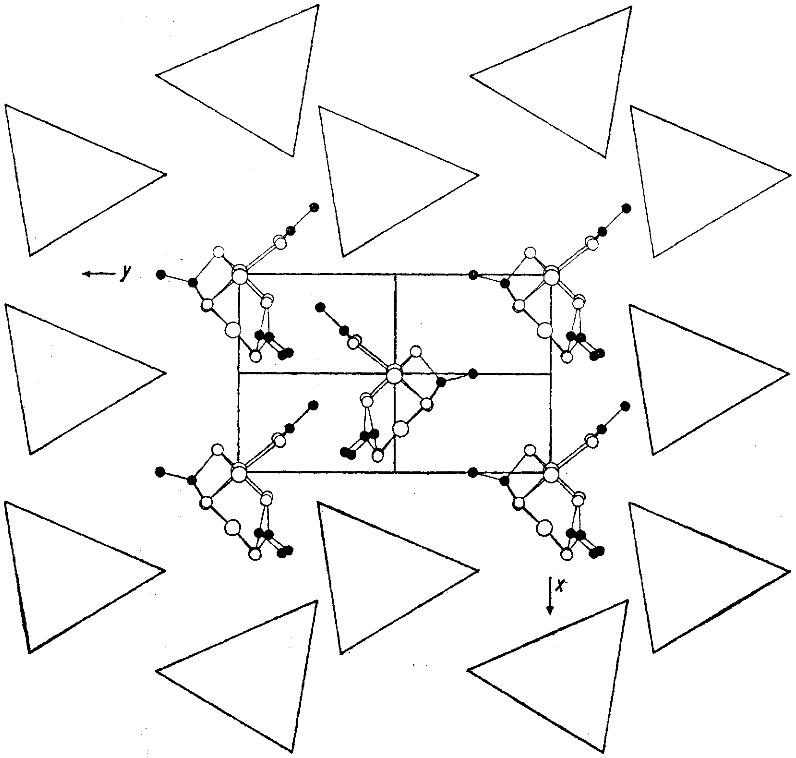

FIGURE 3

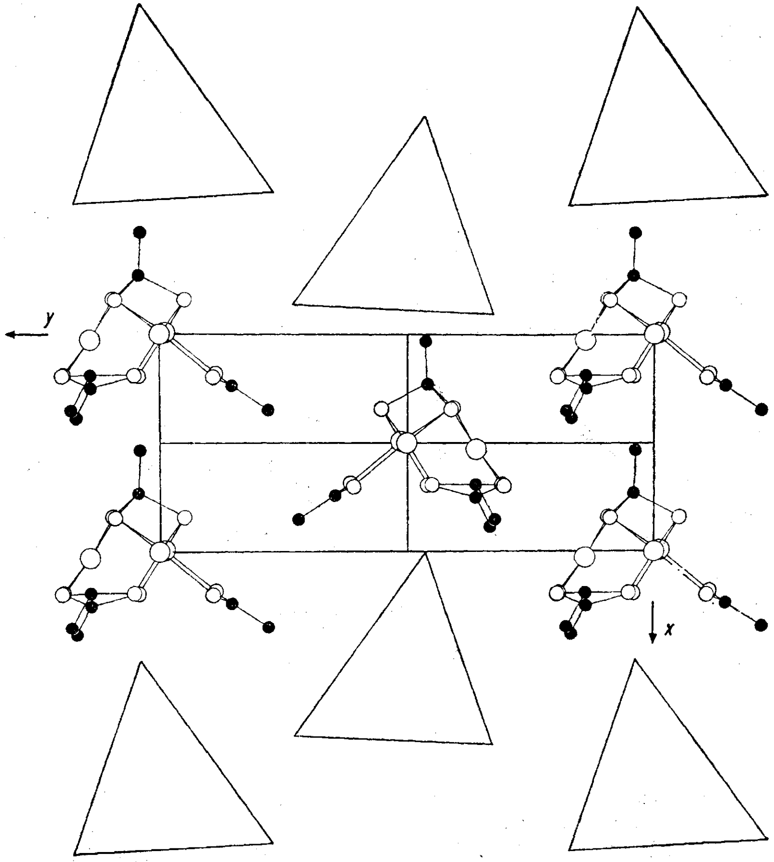

FIGURE 4

programs of the Laboratorio di Strutturistica Chimica del C.N.R.[4,5] Neutral-atom scattering factors were taken from ref. 6, and corrections for the anomalous dispersion of nickel and sulphur from ref. 7.

DISCUSSION

Description of the Structures.—The title compound in both form (I) and form (II) consists of a trigonal pyramid-like structure with the molecular configuration shown in Figure 1. Three nickel atoms, which form a regular triangle with presumably non-bonded nickel–nickel distances of *ca.* 3 Å, are present in the complex unit. This is an example of a transition-metal cluster.

TABLE 3

Bond lengths (Å) and angles (°) in the two crystalline forms

(*a*) Form (I)

(*i*) Distances

Ni(1)–S(1)	2.18(1)	S(2)–C(1)	1.61(1)
Ni(1)–S(6)	2.20(2)	S(3)–C(3)	1.51(1)
Ni(1)–S(7)	2.21(1)	S(4)–C(3)	1.84(1)
Ni(1)–S(9)	2.16(1)	S(5)–C(5)	1.73(3)
Ni(2)–S(2)	2.18(1)	S(6)–C(5)	1.57(3)
Ni(2)–S(3)	2.19(1)	S(7)–C(7)	1.87(4)
Ni(2)–S(7)	2.16(1)	S(8)–C(7)	1.81(2)
Ni(2)–S(8)	2.20(1)	S(9)–C(7)	1.85(4)
Ni(3)–S(4)	2.20(1)	C(1)–C(2)	1.52(4)
Ni(3)–S(5)	2.23(1)	C(3)–C(4)	1.53(2)
Ni(3)–S(8)	2.17(1)	C(5)–C(6)	1.55(4)
Ni(3)–S(9)	2.23(1)	C(7)–C(8)	1.52(2)
S(1)–C(1)	1.83(1)		

(*ii*) Angles

S(1)–Ni(1)–S(6)	88.0(5)	Ni(1)–S(7)–Ni(2)	84.3(4)
S(1)–Ni(1)–S(7)	96.2(6)	Ni(1)–S(7)–C(7)	88(1)
S(1)–Ni(1)–S(9)	173.9(4)	Ni(2)–S(7)–C(7)	89.4(7)
S(6)–Ni(1)–S(7)	174.9(6)	Ni(2)–S(8)–Ni(3)	86.2(3)
S(6)–Ni(1)–S(9)	94.7(6)	Ni(2)–S(8)–C(7)	90(1)
S(7)–Ni(1)–S(9)	80.8(4)	Ni(3)–S(8)–C(7)	89(1)
S(2)–Ni(2)–S(3)	89.1(4)	Ni(1)–S(9)–Ni(3)	85.4(3)
S(2)–Ni(2)–S(7)	97.1(4)	Ni(1)–S(9)–C(7)	90(1)
S(2)–Ni(2)–S(8)	176.7(4)	Ni(3)–S(9)–C(7)	86.3(7)
S(3)–Ni(2)–S(7)	172.7(5)	S(1)–C(1)–S(2)	125.0(5)
S(3)–Ni(2)–S(8)	93.6(3)	S(1)–C(1)–C(2)	110(2)
S(7)–Ni(2)–S(8)	80.1(4)	S(2)–C(1)–C(2)	125(2)
S(4)–Ni(3)–S(5)	88.5(4)	S(3)–C(3)–S(4)	130.1(5)
S(4)–Ni(3)–S(8)	95.7(4)	S(3)–C(3)–C(4)	117(1)
S(4)–Ni(3)–S(9)	176.2(4)	S(4)–C(3)–C(4)	113(1)
S(5)–Ni(3)–S(8)	175.8(4)	S(5)–C(5)–S(6)	131(1)
S(5)–Ni(3)–S(9)	94.8(4)	S(5)–C(5)–C(6)	110(2)
S(8)–Ni(3)–S(9)	81.0(3)	S(6)–C(5)–C(6)	119(2)
Ni(1)–S(1)–C(1)	113.6(4)	S(7)–C(7)–S(8)	99(2)
Ni(2)–S(2)–C(1)	118.2(6)	S(7)–C(7)–S(9)	99(1)
Ni(2)–S(3)–C(3)	118.1(6)	S(7)–C(7)–C(8)	114(3)
Ni(3)–S(4)–C(3)	110.3(5)	S(8)–C(7)–S(9)	103(1)
Ni(3)–S(5)–C(5)	113.0(9)	S(8)–C(7)–C(8)	116(2)
Ni(1)–S(6)–C(5)	116(1)	S(9)–C(7)–C(8)	122(3)

(*b*) Form (II)

(*i*) Distances

Ni(1)–S(1)	2.22(2)	S(2)–C(1)	1.67(3)
Ni(1)–S(6)	2.18(2)	S(3)–C(3)	1.74(5)
Ni(1)–S(7)	2.22(1)	S(4)–C(3)	1.62(5)
Ni(1)–S(9)	2.10(1)	S(5)–C(5)	1.74(3)
Ni(2)–S(2)	2.21(2)	S(6)–C(5)	1.59(3)
Ni(2)–S(3)	2.21(1)	S(7)–C(7)	1.99(5)
Ni(2)–S(7)	2.17(1)	S(8)–C(7)	1.87(2)
Ni(2)–S(8)	2.21(1)	S(9)–C(7)	1.76(5)
Ni(3)–S(4)	2.18(1)	C(1)–C(2)	1.5(1)
Ni(3)–S(5)	2.20(1)	C(3)–C(4)	1.57(3)
Ni(3)–S(8)	2.15(1)	C(5)–C(6)	1.6(1)
Ni(3)–S(9)	2.19(1)	C(7)–C(8)	1.40(4)
S(1)–C(1)	1.69(4)		

TABLE 3 (*Continued*)

(*ii*) Angles

S(1)–Ni(1)–S(6)	89.1(5)	Ni(1)–S(7)–Ni(2)	86.3(5)
S(1)–Ni(1)–S(7)	92.8(6)	Ni(1)–S(7)–C(7)	86(1)
S(1)–Ni(1)–S(9)	173.2(6)	Ni(2)–S(7)–C(7)	89.6(8)
S(6)–Ni(1)–S(7)	175.8(5)	Ni(2)–S(8)–Ni(3)	84.3(3)
S(6)–Ni(1)–S(9)	97.3(6)	Ni(2)–S(8)–C(7)	91(1)
S(7)–Ni(1)–S(9)	80.7(4)	Ni(3)–S(8)–C(7)	89(1)
S(2)–Ni(2)–S(3)	88.8(5)	Ni(1)–S(9)–Ni(3)	87.1(4)
S(2)–Ni(2)–S(7)	95.2(5)	Ni(1)–S(9)–C(7)	96(2)
S(2)–Ni(2)–S(8)	176.9(5)	Ni(3)–S(9)–C(7)	90.5(9)
S(3)–Ni(2)–S(7)	172.9(6)	S(1)–C(1)–S(2)	129(2)
S(3)–Ni(2)–S(8)	94.3(4)	S(1)–C(1)–C(2)	121(3)
S(7)–Ni(2)–S(8)	81.7(4)	S(2)–C(1)–C(2)	109(3)
S(4)–Ni(3)–S(5)	89.6(5)	S(3)–C(3)–S(4)	129(1)
S(4)–Ni(3)–S(8)	94.8(4)	S(3)–C(3)–C(4)	103(3)
S(4)–Ni(3)–S(9)	174.4(5)	S(4)–C(3)–C(4)	128(3)
S(5)–Ni(3)–S(8)	175.4(5)	S(5)–C(5)–S(6)	131(2)
S(5)–Ni(3)–S(9)	95.8(5)	S(5)–C(5)–C(6)	117(2)
S(8)–Ni(3)–S(9)	79.8(4)	S(6)–C(5)–C(6)	112(3)
Ni(1)–S(1)–C(1)	115(1)	S(7)–C(7)–S(8)	96(2)
Ni(2)–S(2)–C(1)	115(2)	S(7)–C(7)–S(9)	97(1)
Ni(2)–S(3)–C(3)	112(1)	S(7)–C(7)–C(8)	127(4)
Ni(3)–S(4)–C(3)	117(1)	S(8)–C(7)–S(9)	101(2)
Ni(3)–S(5)–C(5)	115(1)	S(8)–C(7)–C(8)	115(2)
Ni(1)–S(6)–C(5)	112(1)	S(9)–C(7)–C(8)	117(4)

Two different kinds of ligand are present: at one side of the nickel triangle there are three molecules of dithioacetic acid bridging the metal atoms, and at the other side the three sulphur atoms of the sulphur-substituted ortho-form of dithioacetic acid (see Experimental section) link the nickel atoms. Sulphur atoms are only very approximately equidistant from the nickel atoms so as to give an approximately square-planar environment of four sulphur atoms for each nickel(II) ion.

The idealised C_{3v} symmetry of the complex unit is lowered because the nickel–sulphur bonds Ni(1)–S(7), S(7)–Ni(2), Ni(2)–S(8), S(8)–Ni(3), Ni(3)–S(9), and S(9)–Ni(1), are alternately longer and shorter in both forms, in such a way that the molecular symmetry is closer to C_3.

Although both structures are non-centrosymmetric, and data collected have not been corrected for absorption, it may be noted that the same alternation in NiS bond lengths occurs in both independently determined structures.

Each molecule interacts with its neighbours *via* short Ni · · · S contacts of 3.2 Å [Ni(2) · · · S(5) and Ni(3) · · · S(2)]. In this way both forms produce one-dimensional polymeric systems, developed along the *z*-axis (see Figure 2). Packing in the *xy* planes is, however, different in the two forms (Figures 3 and 4). Form (I) is more compact, consistent with its smaller volume, but in form (II) more rigorous order gives rise to less-efficient packing.

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