Golic, L. & Bulc, N. (1988). *Acta Cryst.* C**44**, 2065–2068.

Hegetschweiler, K., Erni, I., Schneider, W. & Schmalle, H. (1990). *Helv. Chim. Acta*, **73**, 97–105.

Hiller, W. (1990). *HIPAS*. Program generates input files and *hkl* files for *SHELXS*86 and *SHELX*76. Univ. of Tübingen, Germany.

Johnson, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Jurnak, F. & Raymond, K. N. (1974). *Inorg. Chem.* **13**, 2387–2397.

Nardelli, M. (1988). *PARST*88. Program for crystallographic calculations. Univ. of Parma, Italy.

Schneider, W., Erni, I. & Hegetschweiler, K. (1989). European Patent EP 0 190 676 B1.

Schomaker, V. & Marsh, R. E. (1983). *Acta Cryst.* A**39**, 819–820.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS*86. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard. Oxford Univ. Press.

Sheldrick, G. M. (1988). *SHELXTL-Plus*88. *Structure Determination Software Programs*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

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Structure of Bis(thiocyanato-*N*)bis(thiosemicarbazide-N^1,*S*)nickel(II): a Redetermination

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Abstract. $[Ni(NCS)_2(CH_5N_3S)_2]$, M_r = 356·7, monoclinic, $P2_1/c$, a = 5·297 (1), b = 7·869 (1), c = 16·078 (2) Å, β = 91·53 (1)°, V = 669·9 Å^3, Z = 2, D_m = 1·76, D_x = 1·771 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 19·9 cm^{-1}, $F(000)$ = 364, T = 295 K, final R = 0·026 for 1576 significant [$F > 10\sigma(F)$] reflections. The complex lies on a crystallographic centre of symmetry. The Ni atom is octahedrally coordinated by two thiocyanates (through N atoms) and by two thiosemicarbazide molecules (through hydrazinic N and S atoms). The crystal structure is stabilized by N—H···S hydrogen bonds. Early work on this structure [Garaj & Dunaj-Jurco (1968). *Chem. Commun.* p. 518] used photographic data and was refined to R = 0·13 for 512 reflections.

Introduction. Metal complexes of the thiosemicarbazide (TSC) molecule have been widely studied because of their broad pharmacological activity (Akbar Ali & Livingstone, 1974; Campbell, 1975). The activity of TSC and related species is thought to be dependent on metal–chelate formation and has led to the study of a large number of nickel(II) complexes (*e.g.* Lopez-Castro & Truter, 1963). Preparation and magnetic properties (Sirota, Sramko & Kohout, 1966) and structure (Garaj & Dunaj-Jurco, 1968) have previously been reported for the title compound. However, the structure is imprecise (R = 0·13) as the data were recorded photographically (512 reflections). We report here a redetermination based on diffractometer data.

Experimental. The title compound was prepared by decomposing $N_2H_5Ni(N_2H_3COO)_3.H_2O$ (Braibanti, Bigliardi, Lanfredi & Tiripicchio, 1966) in aqueous thiocyanic acid; D_m measured by flotation using a mixture of chloroform and bromoform. Dark blue

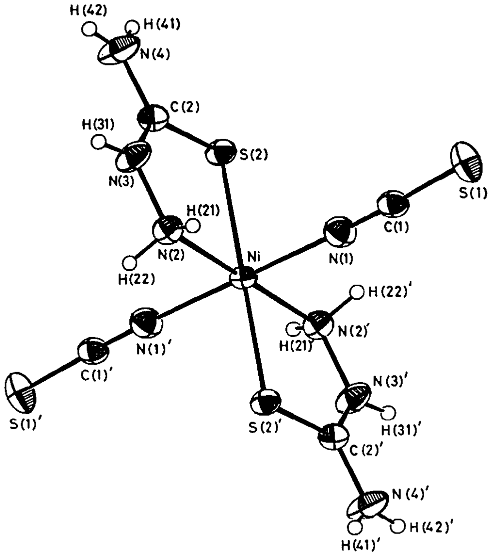

Fig. 1. *ORTEP*II diagram (Johnson, 1976) and atom-numbering scheme. Non-H ellipsoids at 50% probability level. H atoms given arbitrary radii.

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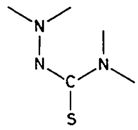
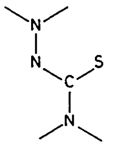
crystal, 0·25 × 0·1 × 0·1 mm, recrystallized from hot water; Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation; cell dimensions by least-squares fit of 25 reflections ($18 \le 2\theta \le 40°$); $2\theta_{\max} = 57°$. Total number of reflections 2540 (ω–2θ mode), unique data 2140 and 1576 observed with $F > 10\sigma(F)$; $0 \le h \le 7$, $0 \le k \le 11$, $-23 \le l \le 23$; Lorentz and polarization corrections, no absorption correction; $R_{\rm int} = 0{\cdot}038$; three standard reflections (233, 148, 257) measured every 100 reflections showed no significant decay. Structure solution by Patterson and Fourier methods. H atoms from $\Delta\rho$ map. Full-matrix least-squares refinement on $|F_o|$, anisotropic for non-H atoms and isotropic for H atoms. Final $R = 0{\cdot}026$ and $wR = 0{\cdot}030$ where $w = 1{\cdot}9247/[\sigma^2(F_o) + 0{\cdot}000311F_o^2]$; $S = 1{\cdot}16$. Final $(\Delta/\sigma)_{\max} = 0{\cdot}001$, $(\Delta\rho)_{\max} = 0{\cdot}34$ and $(\Delta\rho)_{\min} = -0{\cdot}68$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations based on $|F_o|$ using *SHELX76* (Sheldrick, 1976) were carried out on a DEC 1090 computer.

Discussion. The molecular structure of the title compound is shown in Fig. 1. Atomic parameters are given in Table 1.* Bond distances and angles are given in Table 2. The Ni atom, at a centre of symmetry, is octahedrally coordinated by two N-thiocyanato ligands and by two chelating TSC molecules.

Free TSC is known to adopt a *trans* configuration, the non-H atoms being essentially coplanar (*a*). However, the only complexes so far known to contain TSC in this configuration are polymeric Ag$^{\rm I}$ complexes (Campbell, 1975). Here, as in all other complexes, TSC is observed to adopt a *cis* configuration (*b*) and is bidentate, bonding through sulfur and the hydrazinic nitrogen.



(*a*)



(*b*)

Here, the Ni—S(2) distance is 2·4285 (5) Å, shorter than in nickel–thiourea complexes (Wilkinson, Gillard & McCleverty, 1987). The TSC molecule is essentially planar with the nickel atom 0·161 (1) Å away from this plane. The angle between the plane N(2)N(3)C(2)S(2) and the plane N(2)NiS(2) is 5·71 (5)°, considerably higher than the value of 1·5° observed in *trans*-$[\mathrm{Ni(N_2H_3{-}CS{-}NH_2)_2(H_2O)_2](NO_3)_2}$ (Hazell, 1968). There are no significant changes in the bond lengths N(2)—N(3) [1·415 (2) Å] and C(2)—S(2) [1·709 (2) Å] upon coordination, the corresponding values for free TSC being 1·411 (2) and 1·707 (2) Å, respectively (Andreetti, Domiano, Gasparri, Nardelli & Sgarabotto, 1970). The thiocyanate group has N(1)—C(1)—S(1) = 177·7 (2)° and Ni—N(1)—C(1) = 177·8 (2)°. The Ni—N(1) bond length [2·071 (2) Å] is identical to the 2·07 Å observed in *trans*-$\mathrm{Ni(NCS)_2(NH_3)_4}$ (Yukhno & Porai-Koshits, 1957). Crystal packing is stabilized by the N—H···S intermolecular hydrogen bonds listed in Table 2.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for the title compound*

$$U_{\rm eq} = (1/3)\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni	0·0	0·0	0·0	0·0195 (1)
N(1)	0·2318 (3)	0·1864 (2)	0·0514 (1)	0·0296 (7)
C(1)	0·3619 (3)	0·2874 (2)	0·0824 (1)	0·0242 (6)
S(1)	0·5523 (1)	0·4251 (1)	0·12872 (4)	0·0354 (2)
N(2)	0·2247 (3)	−0·1935 (2)	0·0519 (1)	0·0254 (6)
N(3)	0·1399 (3)	−0·2605 (2)	0·1279 (1)	0·0312 (7)
C(2)	−0·0527 (4)	−0·1943 (2)	0·1670 (1)	0·0243 (6)
S(2)	−0·2215 (1)	−0·0242 (1)	0·12978 (3)	0·0236 (2)
N(4)	−0·1129 (4)	−0·2628 (3)	0·2391 (1)	0·0417 (8)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen bonding in the title compound*

Ni—N(1)	2·071 (2)	N(2)—N(3)	1·415 (2)
Ni—N(2)	2·093 (2)	C(2)—N(3)	1·320 (3)
Ni—S(2)	2·429 (1)	C(2)—N(4)	1·325 (2)
N(1)—C(1)	1·156 (2)	C(2)—S(2)	1·709 (2)
C(1)—S(1)	1·645 (2)		

N(1)—Ni—N(2)	91·8 (1)	N(1)—C(1)—S(1)	177·7 (2)
N(1)—Ni—S(2)	90·4 (1)	N(2)—N(3)—C(2)	122·1 (2)
N(2)—Ni—S(2)	83·3 (1)	N(3)—C(2)—N(4)	117·6 (2)
Ni—N(1)—C(1)	177·8 (2)	N(3)—C(2)—S(2)	123·1 (1)
Ni—N(2)—N(3)	115·2 (1)	N(4)—C(2)—S(2)	119·3 (2)
Ni—S(2)—C(2)	95·9 (1)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(2)—H(21)···S(2^a)	0·88 (4)	2·59 (4)	3·428 (2)	158 (3)
N(3)—H(31)···S(1^b)	0·83 (5)	2·54 (4)	3·300 (2)	153 (4)
N(2)—H(22)···S(1^c)	0·87 (3)	2·91 (3)	3·651 (2)	144 (3)
N(4)—H(41)···S(1^d)	0·83 (4)	2·71 (4)	3·519 (2)	166 (3)
N(4)—H(42)···S(2^d)	0·80 (4)	2·63 (4)	3·408 (2)	165 (3)

Symmetry codes: (*a*) $1 + x, y, z$; (*b*) $x, -1 + y, z$; (*c*) $1 - x, -y, -z$; (*d*) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$.

References

Akbar Ali, M. & Livingstone, S. E. (1974). *Coord. Chem. Rev.* **13**, 101–132.

Andreetti, G. D., Domiano, P., Gasparri, G. F., Nardelli, M. & Sgarabotto, P. (1970). *Acta Cryst.* **B26**, 1005–1009.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54117 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Braibanti, A., Bigliardi, G., Lanfredi, A. M. & Tiripicchio, A. (1966). *Nature (London)*, **211**, 1174–1175.
Campbell, M. J. M. (1975). *Coord. Chem. Rev.* **15**, 279–319.
Garaj, J. & Dunaj-Jurco, M. (1968). *Chem. Commun.* p. 518.
Hazell, R. G. (1968). *Acta Chem. Scand.* **22**, 2809–2816.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lopez-Castro, A. & Truter, M. R. (1963). *J. Chem. Soc.* pp. 1309–1317.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sirota, A., Sramko, T. & Kohout, J. (1966). *Chem. Zvesti*, **20**, 752–62. [*Chem. Abstr.* **66** 81991m.]
Wilkinson, G., Gillard, R. D. & McCleverty, J. A. (1987). Editors. *Comprehensive Coordination Chemistry*, Vol. 2, p. 639. Oxford: Pergamon Press.
Yukhno, E. K. & Porai-Koshits, M. A. (1957). *Kristallografiya*, **2**, 239–248.

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Structure of (μ_3-CCl)$Co_3(CO)_7$(μ-dppm); a Chloroalkylidyne Capped Tricobalt Cluster with a Bidentate Bis(diphenylphosphino)methane Ligand Bridging One Edge of the Tricobalt Triangle

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Abstract. Heptacarbonyl-μ_3-chloromethylidyne-μ_2-[methanediylbis(diphenylphosphino)-*P*,*P*′]tricobalt-(3*Co*–*Co*) isopentane solvate, $[Co_3(CCl)(C_{25}H_{25}P_2)(CO)_7].C_5H_{12}$, $M_r = 876{\cdot}83$, triclinic, $P\bar{1}$, $a = 12{\cdot}050\,(6)$, $b = 12{\cdot}758\,(6)$, $c = 13{\cdot}076\,(6)$ Å, $\alpha = 95{\cdot}88\,(3)$, $\beta = 101{\cdot}12\,(3)$, $\gamma = 100{\cdot}55\,(3)°$, $V = 1919\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}52$, D_m(flotation) = $1{\cdot}49$ g cm^{-3}, λ(Mo $K\alpha$) = $0{\cdot}7107$ Å, μ(Mo $K\alpha$) = $14{\cdot}71$ cm^{-1}, $F(000) = 892$, $T = 295$ K, $R = 0{\cdot}054$ for 4774 independent reflections with $I > 3\sigma(I)$. (μ_3-CCl)$Co_3(CO)_7$(μ-dppm) is the product of the reaction of bis(diphenylphosphino)methane (dppm) and chloroalkylidynenonacarbonyltricobalt (μ_3-CCl)$Co_3(CO)_9$. A disordered solvent molecule (isopentane) was included in the calculations using back Fourier transform methods. The structure contains a triangle of Co atoms capped by the chloroalkylidyne unit, and with one of the edges of the Co triangle bridged by the dppm unit. The Co—Co distances range from 2·483 (1) to 2·492 (1) Å. The other dimensions of major interest are Co—P 2·200 (3) Å and Co—C(Cl) which range from 1·901 (5) to 1·858 (3) Å.

Introduction. (μ_3-CCl)$Co_3(CO)_7$(μ-dppm) (1) is one of a number of alkylidene tricobalt clusters containing a bidentate phosphine ligand synthesized recently (Downard, Robinson & Simpson, 1986; Balavione, Collin, Bonnet & Lavigne, 1985; Aime, Botta, Gobetto, Osella & Molone, 1987; Bruce, Kehoe, Matisons, Nicholson, Rieger & Williams, 1982). Few have been fully characterized by X-ray crystallography. This paper reports the crystal and molecular structure of (1) synthesized by the benzophenone ketyl radical anion catalyzed reaction of (μ_3CCl)$Co_3(CO)_9$ with dppm. The structure can be compared with the methyl analogue (2), the structure of which has been determined twice (Balavione *et al.*, 1985; Downard *et al.*, 1986). Values given here for (2) are mean values unless otherwise stated.

Experimental. (μ_3-CCl)$Co_3(CO)_7$(μ-dppm) crystallizes as black crystals (Bruce *et al.*, 1982). An irregular crystal of maximum dimensions 0·28 × 0·29 × 0·09 mm was mounted on a quartz fiber and the lattice parameters ($T = 295$ K, 24 reflections θ range 18–23°) were determined and refined with the least-squares routine on an Enraf–Nonius CAD-4 four-circle diffractometer equipped with a graphite monochromator.

A total of 6741 unique reflections (6917 measured reflections) were collected in the range $1{\cdot}50 < \theta < 25{\cdot}0°$ using an ω–2θ scan mode. $-14 < h < 13$, $-15 < k < 15$, $0 < l < 15$. The intensity of one standard reflection was measured after every 2000 s of X-ray exposure. Approximately 17% decomposition occurred during data collection. Lorentz, polarization and absorption corrections (Gaussian integration method, maximum and minimum transmission factors were 0·874 and 0·679 respectively) were applied to all reflections using locally written programs. 4774 independent reflections with $I > 3\sigma(I)$ were used in the structure refinement calculations (on *F*) using *RAELS*88 (Rae, 1984). Scattering factors for neutral atoms were obtained from Ibers & Hamilton (1974).

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