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Structure of the Beta Form of Bis(diethyldithiocarbamato)nickel(II)

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Abstract. [Ni($C_5H_{10}NS_2$)$_2$], $M_r = 355 \cdot 25$, tetragonal, $P4_2/n$ (No. 86), $a = 16 \cdot 244$ (3), $c = 6 \cdot 327$ (1) Å, $V = 1669 \cdot 4$ (7) Å^3, $Z = 4$, $D_x = 1 \cdot 41$ g cm^{-3}, λ(Mo $K\alpha$) $= 0 \cdot 71073$ Å, $\mu = 16 \cdot 32$ cm^{-1}, $F(000) = 743 \cdot 87$, $T = 298$ K. Convergence to final conventional R values of $R = 0 \cdot 0321$ and $wR = 0 \cdot 0370$ was obtained using 79 variable parameters and 1105 reflections with $|F_o|^2 > 3\sigma(|F_o|^2)$. The unit cell consists of four discrete bis(diethyldithiocarbamato)Ni^{II} molecules. Each four-coordinate square-planar Ni^{II} center is bonded to four S atoms of two chelating diethyldithiocarbamate ligands. The Ni, two N and four S atoms of each discrete unit lie in the same plane. The Ni—S distances are 2·204 (1) and 2·192 (1) Å, the C—S distances are 1·711 (3) and 1·725 (3) Å.

Introduction. The diethyldithiocarbamate ligand, [$S_2CN(C_2H_5)_2$]$^-$ (dtc), gives metal complexes with a wide variety of transition metals. Our continued interest (Fackler, Niera, Campana & Trzcinska-Bancroft, 1984) in the dithiocarbamate ligand centers around its ability to stabilize Ni^{IV} (Fackler, Avdeef & Fischer, 1973), an unusual oxidation state of Ni. The ability of the dithiocarbamate ligand to delocalize positive charge from the metal center is believed to be an important factor in the chemistry of this ligand. In addition to monomeric complexes of dithiocarbamate, dimeric systems have been characterized. Calabro, Harrison, Palmer, Moguel, Rebbert & Burmeister (1981) report the observation of an Au^{II} dithiocarbamate dimer complex upon oxidation of [Au(dtc)]$_2$ with Br$_2$ at low temperatures.

There are three known modifications of bis(diethyldithiocarbamato)Ni^{II}. The monoclinic α form (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965) is the stable modification, while there are two less-stable tetragonal forms, β and γ (Vaciago & Fasana, 1958). In the course of our work extending the chemistry of dtc to trimeric systems we isolated the β form of [Ni{$S_2CN(C_2H_5)_2$}$_2$], [Ni(dtc)$_2$]. In this paper we report the determination of the crystal structure of the β modification of bis(diethyldithiocarbamato)nickel, [Ni{$S_2CN(C_2H_5)_2$}$_2$], obtained from the reaction of an Ni^{II} salt with sodium diethyldithiocarbamate. As judged by the e.s.d.'s of the fractional positional parameters as well as those of the distances and angles, the structure reported here is far more precise than the report by Bonamico *et al.* (1965) (monoclinic; $P2_1/c$, $a = 6 \cdot 189$, $b = 11 \cdot 537$, $c = 11 \cdot 603$ Å, $\beta = 95°51'$, $R = 0 \cdot 101$) for the structure of the α form.

Experimental. The complex bis(diethyldithiocarbamato)nickel was obtained from a reaction of sodium diethyldithiocarbamate, Na(dtc), with a nickel octanoate/ethyl borate mixture. The crystals were grown by slow evaporation of the product from a solution of THF/CHCl$_3$/Et$_2$O.

Single multi-faceted green crystal of approximate dimensions $0 \cdot 25 \times 0 \cdot 20 \times 0 \cdot 25$ mm mounted in a random orientation on a glass fiber. Tetragonal symmetry suggested on the basis of interaxial angles and confirmed by a Delaunay reduction. Axial lengths checked by comparison with the interlayer spacings observed in axial photographs. Refined cell parameters obtained from the setting angles of 19 reflections with $10 < 2\theta < 25°$. Data collection carried out at room

temperature using the Wyckoff ω-scanning technique in bisecting geometry (Nicolet $P3$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation). Intensities measured for 1479 unique reflections, 1105 with $|F_o|^2 > 3\sigma(|F_o|^2)$ ($h \leq 19$, $k \leq 19$, $l \leq 8$) with $3 < 2\theta < 50°$. Scan rate variable, 4–29.30° min^{-1}; scan range $-1.0°$ in ω from $K\alpha_1$ to $+1.0°$ from $K\alpha_2$. Backgrounds estimated from a 96-step peak profile. Three standards (840, 131, 451) measured every 47 data. The data were corrected for decay ($\sim$0.02) by scaling on the three standards which all decayed similarly, data were also corrected for absorption, Lorentz and polarization effects. Corrections for absorption applied empirically on the basis of azimuthal scans of six reflections spanning a range of 2θ values from 6.91 to 42.40° (minimum and maximum transmission 0.135 and 0.167, respectively). Crystal solution and refinement carried out using the SHELXTL collection of crystallographic software (Sheldrick, 1981). The Ni- and S-atom positions determined from direct methods (SOLV, a program adapted from MULTAN78; Main, Hull, Lessinger, Germain, Declercq & Woolfson); all remaining atoms located on difference Fourier maps refined anisotropically, H atoms assigned common U factor. Refinement based on F with weights of the form $w^{-1} = (\sigma^2|F_o| + |0.00116|F_o^2)$. The value 0.00116, g, was refined by fitting $(F_o - F_c)^2$ to $[\sigma^2(F) + gF^2]/k$ (k = scale factor) to put weights on an approximately

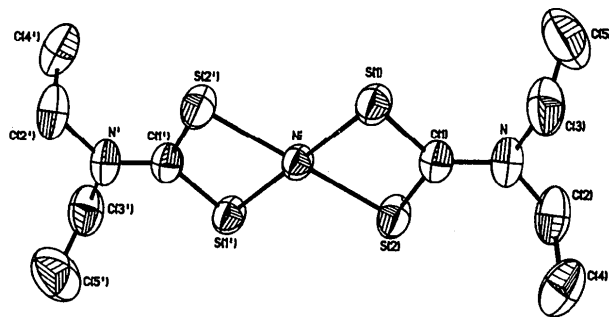Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}*
Ni	10000	5000	0	44 (1)
S(1)	9227 (1)	4676 (1)	2739 (1)	55 (1)
S(2)	8781 (1)	5342 (1)	−1203 (1)	61 (1)
C(1)	8423 (2)	5010 (2)	1217 (5)	48 (1)
N	7641 (2)	5017 (2)	1774 (5)	57 (1)
C(2)	6998 (2)	5359 (3)	397 (7)	73 (2)
C(3)	7386 (3)	4684 (3)	3842 (6)	77 (2)
C(4)	6903 (3)	6270 (3)	680 (9)	93 (2)
C(5)	7162 (3)	3788 (3)	3733 (10)	117 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Ni–S(1)	2.204 (1)	Ni–S(2)	2.192 (1)
S(1)–C(1)	1.711 (3)	S(2)–C(1)	1.725 (3)
C(1)–N	1.319 (4)	N–C (2)	1.468 (5)
N–C(3)	1.475 (5)	C(2)–C(4)	1.499 (6)
C(3)–C(5)	1.501 (7)		
S(1)–Ni–S(2)	79.6 (1)	S(1)–Ni–S(1')	180.0 (1)
S(2)–Ni–S(1')	100.4 (1)	Ni–S(1)–C(1)	85.2 (1)
Ni–S(2)–C(1)	85.3 (1)	S(1)–C(1)–S(2)	110.0 (2)
S(1)–C(1)–N	126.0 (3)	S(2)–C(1)–N	124.0 (3)
C(1)–N–C(2)	122.0 (3)	C(1)–N–C(3)	120.2 (3)
C(2)–N–C(3)	117.7 (3)	N–C(2)–C(4)	112.0 (3)
N–C(3)–C(5)	112.5 (4)		

absolute scale. Neutral-atom scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974). Convergence to conventional R values of $R = 0.0321$ and $wR = 0.0370$ obtained using 79 variable parameters and 1105 reflections with $|F_o|^2 > 3\sigma|F_o|^2$. For final cycle maximum shift/e.s.d. $= 0.019$ with a goodness-of-fit indicator of 1.143. Residual electron density on final difference Fourier map of $+0.22$ and -0.32 e Å^{-3} in the vicinity of C(5).

Fig. 1. A perspective view of the [Ni{S$_2$NC(C$_2$H$_5$)$_2$}$_2$], [Ni(dtc)$_2$], structure. Thermal ellipsoids have been drawn at the 50% probability level. H atoms have not been included.

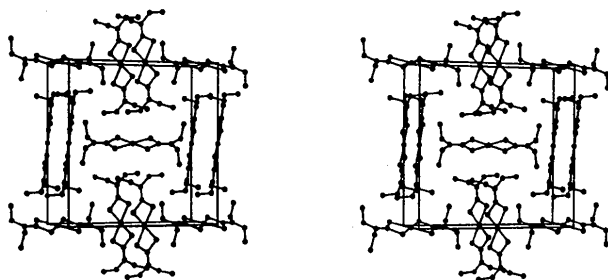Fig. 2. A stereoview packing diagram viewed down the c axis. H atoms have not been included.

Discussion. The product obtained from the reaction of an Ni^{II} salt and sodium diethyldithiocarbamate and isolated in the solid state *via* slow evaporation of a mixed solvent of THF/CHCl$_3$/Et$_2$O was the β form of bis(diethyldithiocarbamato)nickel, [Ni(dtc)$_2$]. The title complex consists of one Ni^{II} center in a four-coordinate square-planar geometry. Ni^{II} is S-bonded by two chelating diethyldithiocarbamate ligands. A perspective view of the complex is shown in Fig. 1. A stereoview packing diagram of the cell contents projected down the c axis is shown in Fig. 2. Atomic positional and equivalent isotropic thermal parameters for all non-H atoms are presented in Table 1.* Bond angles and distances are summarized in Table 2.

All of the atoms of the discrete complex described here ($[Ni\{S_2CN(CH_2CH_3)_2\}_2]$ in the solid state, β form), apart from the methyl groups, lie approximately in a plane. The deviation from the least-squares fit of all the atoms to the plane, excluding the CH_3 groups, is quite small with a maximum deviation of 0.039 Å for C(3).

Of particular interest are the Ni—S, S—C and C—N bond lengths. The Ni—S distances [2.204 (1) and 2.192 (1) Å] are similar to those reported for the α form (Bonamico et al., 1965), 2.207 (2) and 2.195 (2) Å. As compared to the Ni—S distances of the cation tris(di-n-butyldithiocarbamato)Ni^{IV}, $[Ni\{S_2CN-(C_4H_9)_2\}_3]^+$, reported by Fackler et al. (1973), 2.261 (1) Å, the Ni—S distances observed here are approximately 0.06 Å shorter. The observation that four-coordinate NiS_4 cores have somewhat shorter Ni—S bonds than do NiS_6 cores has been previously noted (Bonamico et al., 1965). The S—C bond lengths observed here, 1.711 (3) and 1.725 (3) Å, compare well with those of the α form, 1.713 (7) and 1.700 (7) Å. Similar S—C distances are reported for thiourea derivatives and coordination complexes thereof (Lopez-Castro & Truter, 1963; Dias & Truter, 1964) and are considered consistent with an S—C(sp^2) formulation. The C—N bond distance observed for the β form, 1.319 (4) Å, is only slightly shorter than the 1.33 (1) Å reported for the α form. As discussed (Bonamico et al., 1965) this C—N bond has considerable double-bond character. Indeed, it is the significant contribution of the thioureide form (Fackler, 1976) which is believed to lend stability to unusual oxidation of some metal centers, i.e. Au^{II}, Ni^{IV} (Calabro et al., 1981; Fackler et al., 1973) and stabilize M—C bonds by minimizing the importance of the radical pathway for metal–carbon dissociation (Stein, Fackler, Paparizos & Chen, 1981).

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(4-Dimethylaminopyridine)tris(η-methylcyclopentadienyl)uranium(III)

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Abstract. [$U(C_6H_7)_3(C_7H_{10}N_2)$], $M_r = 597.57$, triclinic, $P\bar{1}$, $a = 15.541$ (6), $b = 17.155$ (7), $c = 10.303$ (4) Å, $\alpha = 106.83$ (4), $\beta = 106.52$ (4), $\gamma = 67.04$ (4)°, $V = 2374.7$ Å^3, $Z = 4$, $D_x = 1.671$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 64.9$ cm^{-1}, $F(000) = 1148$, $T = 296$ K, $R = 0.033$ for 3258 independent reflections with $F^2 >$ $3\sigma(F^2)$. Two independent but chemically similar molecules are found in the unit cell. U^{III} is at the center of a distorted tetrahedron consisting of the pyridine N atom and the centroids of the three cyclopentadienyl rings. Distances are: U—N 2.662 (13) and 2.627 (12) Å; av. U—C(ring), 2.82 (4) Å; av. U—Cp, 2.56 (2) Å.