

The Determination of the Crystal Structure of Nickel Ethylenedithiodiacetate Dihydrate (NEDDD)

BY J. PODLAHOVÁ AND J. LOUB

Department of Inorganic Chemistry, Charles University, Albertov 2030, Prague 2, Czechoslovakia

AND C. NOVÁK

Institute of Solid State Physics, Czechoslovak Academy of Sciences, Cukrovarnická 10, Prague 6, Czechoslovakia

(Received 30 November 1971)

The crystal structure of NEDDD, $\begin{array}{c} \text{CH}_2\text{SCH}_2\text{COO} \\ | \\ \text{CH}_2\text{SCH}_2\text{COO} \end{array} \text{Ni} \cdot 2\text{H}_2\text{O}$, has been determined from three-dimensional X-ray data. The unit cell is tetragonal, space group $P4_12_12$ (or $P4_32_12$) with $a=7.238$, $c=20.32$ Å, and contains four molecules. A refinement has led to a final R value of 0.085 for 656 independent reflexions. Two *cis* sulphur atoms, two *trans* carboxylic oxygen atoms and two *cis* water molecules in a slightly distorted octahedral arrangement make up the coordination sphere of the nickel ion. The relevant distances are Ni-S, 2.44 Å; Ni-O(carboxylic), 2.01 Å; Ni-O(water), 2.04 Å.

Introduction

In a study of metal complexes of thiopolycarboxylic acids as sulphur analogues of complexons, spectral and magnetic data indicated the presence of sulphur-metal bonding and an octahedral environment around a metal ion (Podlaha & Podlahová, 1970, 1971). The X-ray crystal structure determination of one typical representative of these compounds, namely NEDDD, was therefore undertaken in order to verify this. Preliminary results of this work have already been published (Loub & Podlahová, 1971).

Experimental

Single crystals of $\text{Ni}(\text{CH}_2\text{SCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were grown from a solution containing 20 millimoles of nickel sulphate and 20 millimoles of sodium ethylenedithiodiacetate per litre of water. They were bright green and prismatic and were stable in air. Two water molecules were evolved at 160°C and decomposition of the organic anion takes place at 190°C.

Lattice constants from rotation and Weissenberg photographs (camera $D=57.3$ mm) at 20°C are $a=7.238 \pm 4$, $c=20.32 \pm 1$ Å. Radiation for intensity measurements: Cu $K\alpha$, $\lambda=1.5418$ Å, Ni filter. The number of molecules in the unit cell is $Z=4$, due to the symmetry of the molecule and the special position of the Ni atoms. Density $D_x=1.89$, $D_{\text{exp}}=1.88 \pm 2$ (pycnometric).

Systematic absences: $00l$ for $l \neq 4n$; $h00$ for $h \neq 2n$. Possible space groups are $P4_12_12$ and $P4_32_12$. The structure is described in $P4_12_12$.

Specimens of about 0.4 mm in three normal directions were selected for Weissenberg equi-inclination photographs hkL ($L=0$ to 12) and Hkl ($H=0$ to 4). The total number of photographs was 18. An absorp-

tion correction $\mu=61.3 \text{ cm}^{-1}$ was used, and a spherical shape for the specimen was supposed with radii $R=0.0202$ and 0.0208 cm for the data from the hkL and Hkl photographs respectively. The correction was linearly interpolated from *International Tables for X-ray Crystallography* (1962a) the respective minima being 3.76 and 3.87.

The intensities were measured visually and the intensity scale was derived from the specimen investigated with a time ratio of 5:4 for successive exposures. The intensities of unobserved reflexions were defined as half the minimum observed intensity in the relevant region of the given photograph. There were 3505 measured reflexions in the range of $\sin \theta/\lambda \leq 0.61 \text{ \AA}^{-1}$. The number of independent reflexions is 656; among them are 45 unobserved reflexions. This represents 72% of reflexions accessible.

Structure determination and refinement

The heavy-atom method was used. The three-dimensional Patterson synthesis yielded the position of Ni and S atoms; from the repeated three-dimensional Fourier synthesis the positions of the rest of the atoms (with the exception of the hydrogen atoms) were known with $R=0.182$. The value of R after subsequent least-squares refinement of 18 scale factors, 8 atom positions and individual isotropic thermal vibration factors reduced to 0.144. After the correction of the atomic scattering factor of Ni for anomalous scattering and the reduction of the F_{obs} values to a single scale factor R was 0.139. Finally after the correction of 15 strong reflexions for extinction, after averaging the equivalent F_{obs} values, which up to this time were handled independently, having been measured on different photographs, and after anisotropic thermal vibration refinement, R decreased to 0.085. The total number of least-

Table 1. Observed and calculated structure factors

The headings of the columns are $h, k, 10|F_o|, 10|F_c|$. + indicates unobserved reflexions; - indicates the reflexions not included in the last least-squares refinement. E denotes the reflexions corrected for extinction.

h	k	$10 F_o $	$10 F_c $
L=0	0	351	357
0	0	847	824
0	0	22	25
0	0	125	105
0	0	500	243
0	0	134	140
0	0	560	456
0	0	395	396
0	0	1790	857
0	0	817	808
0	0	26	6
0	0	266	222
0	0	91	90
0	0	647	868
0	0	436	411
0	0	111	75
0	0	47	87
0	0	454	422
0	0	669	676
0	0	285	276
0	0	23	24
0	0	242	245
0	0	28	24
0	0	104	100
0	0	393	383
0	0	6	6
0	0	413	430
L=1	0	234	220
0	1	568	595
0	1	381	311
0	1	128	101
0	1	327	321
0	1	289	269
0	1	148	172
0	1	86	73
0	1	254	261
0	1	245	245
0	1	104	106
0	1	329	355
0	1	159	153
0	1	352	344
0	1	324	324
0	1	124	125
0	1	411	377
0	1	310	300
0	1	621	567
0	1	305	289
0	1	262	218
0	1	407	376
0	1	111	113
0	1	737	657
0	1	197	218
0	1	100	94
0	1	231	240
0	1	182	182
0	1	165	162
0	1	118	110
0	1	185	182
0	1	117	113
0	1	29	25
0	1	245	188
0	1	283	275
0	1	268	259
0	1	145	146
0	1	6	6
L=2	0	1453	1470
0	0	895	886
0	0	228	259
0	0	252	226
0	0	591	488
0	0	148	134
0	0	43	10
0	0	306	308
0	0	51	58
0	0	638	645
0	0	63	62
0	0	561	566
0	0	360	357
0	0	139	155
0	0	152	159
0	0	138	151
0	0	657	552
0	0	717	743
0	0	101	252
0	0	613	556
0	0	134	299
0	0	190	183
0	0	59	118
0	0	364	408
0	0	693	681
0	0	89	89
0	0	232	217
0	0	165	181
0	0	136	134
0	0	51	60
0	0	180	189
0	0	161	169
0	0	82	102
0	0	180	178
0	0	192	179
0	0	201	196
0	0	154	151

squares refinement cycles was 7; during the refinement 13 unobserved and 10 observed reflexions, which had the calculated to observed value ratio less than 0.5 or exceeding 2.0, were eliminated.

Computer programs: Three-dimensional Patterson and Fourier synthesis (Hadinec, 1969), ORFLS

Table 3. Intramolecular bond distances (Å) and angles (degrees) in the molecule with estimated standard deviations in parentheses

Distances corrected for thermal vibration are also given. ' indicates the equivalent position $1-y, 1-x, \frac{1}{2}-z$ relative to the reference asymmetric unit at x, y, z .

	Uncorrected	Corrected for thermal motion
Ni—S(1)	2.443 (2)	2.456
Ni—O(1)	2.014 (7)	2.032
Ni—O(3)	2.036 (7)	2.055
S(1)—C(1)	1.800 (10)	1.822
S(1)—C(2)	1.819 (11)	1.839
C(1)—C(1')	1.492 (19)	1.526
C(2)—C(3)	1.534 (13)	1.568
C(3)—O(1)	1.255 (13)	1.292
C(3)—O(2)	1.221 (12)	1.263
S(1)—Ni—S(1')	87.1 (1)	
S(1)—Ni—O(1)	92.5 (2)	
S(1)—Ni—O(1)	83.1 (2)	
S(1)—Ni—O(3)	89.1 (2)	
S(1)—Ni—O(3')	169.5 (2)	
O(1)—Ni—O(3)	87.3 (3)	
O(1)—Ni—O(1')	174.0 (5)	
O(1)—Ni—O(3)	96.7 (3)	
O(3)—Ni—O(3')	96.2 (4)	
S(1)—C(1)—C(1')	114.8 (6)	
C(1)—S(1)—C(2)	102.0 (5)	
S(1)—C(2)—C(3)	114.2 (7)	
C(2)—C(3)—O(1)	116.7 (9)	
C(2)—C(3)—O(1)	118.9 (9)	
O(2)—C(3)—O(1)	124.3 (9)	

Table 4. Root-mean-square amplitudes (Å) of vibration along principal thermal ellipsoid axes with e.s.d. in parentheses

Atom	Axis 1	Axis 2	Axis 3
Ni	0.078 (6)	0.104 (4)	0.140 (3)
S(1)	0.064 (8)	0.129 (5)	0.181 (4)
O(1)	0.118 (14)	0.140 (13)	0.191 (12)
O(2)	0.107 (15)	0.137 (14)	0.249 (12)
O(3)	0.091 (17)	0.120 (14)	0.206 (11)
C(1)	0.099 (22)	0.132 (18)	0.197 (16)
C(2)	0.088 (25)	0.150 (18)	0.211 (16)
C(3)	0.096 (23)	0.129 (18)	0.170 (17)

Table 2. Final fractional atomic coordinates and anisotropic thermal parameters ($\times 10^4$) with estimated standard deviations in parentheses

The temperature factor is of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	4(a)	5228 (2)	4772	2500	54 (2)	54	4 (1)	13 (3)	4 (1)
S(1)	8(b)	4323 (4)	7328 (4)	3216 (1)	107 (5)	77 (4)	2 (1)	26 (4)	6 (1)
O(1)	8(b)	6929 (11)	6680 (10)	2108 (3)	67 (13)	124 (16)	9 (2)	7 (11)	-3 (4)
O(2)	8(b)	7522 (12)	9574 (10)	1877 (4)	45 (12)	177 (18)	16 (2)	14 (13)	4 (4)
O(3)	8(b)	6988 (10)	3875 (11)	3213 (3)	66 (12)	126 (15)	7 (1)	42 (12)	10 (4)
C(1)	8(b)	2126 (15)	7956 (16)	2866 (5)	87 (21)	108 (21)	7 (2)	47 (16)	3 (5)
C(2)	8(b)	5859 (17)	9034 (14)	2852 (4)	160 (25)	61 (17)	8 (2)	19 (18)	9 (6)
C(3)	8(b)	6827 (14)	8381 (14)	2222 (5)	64 (18)	85 (19)	7 (2)	18 (15)	-9 (5)

(Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964).

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962b) for S (16.00), O (8.00) and C (6.00). For the atomic scattering factor of Ni^{2+} (26.00) the anomalous scattering correction $\Delta f' = -3.2$ (Cromer, 1965) was used in the whole range of $\sin \theta/\lambda$. The correction of F_{obs} for extinction was carried out according to Smith (1969); the secondary-extinction coefficient (Zachariasen, 1963) used was $g = 4 \times 10^{-5}$. The maximum percentage change was 31% for $F(102)$.

During the least-squares refinement $\sum w(F_o - F_c)^2$ was minimized with the Cruickshank weight (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), $w = 1/(a + |F_o| + c|F_c|)^2$ where $a = 3.6$ and $c = 0.1$. In addition to $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ the least-squares program yielded $R_w = \sum w(F_o - F_c)^2 / \sum w F_o^2$ whose final value was 0.113.

From the 45 unobserved reflexions 32 were used in the final least-squares cycle with the worst agreement for $F(7,1,14)$ (2.6 observed, 5.0 calculated).

Results and discussion

Table 1 contains the observed and calculated structure factors from the final refinement cycle, Table 2, the final atomic positions and anisotropic thermal parameters and Table 3, the calculated intramolecular atomic distances and bond angles. In Table 4 the root-mean-

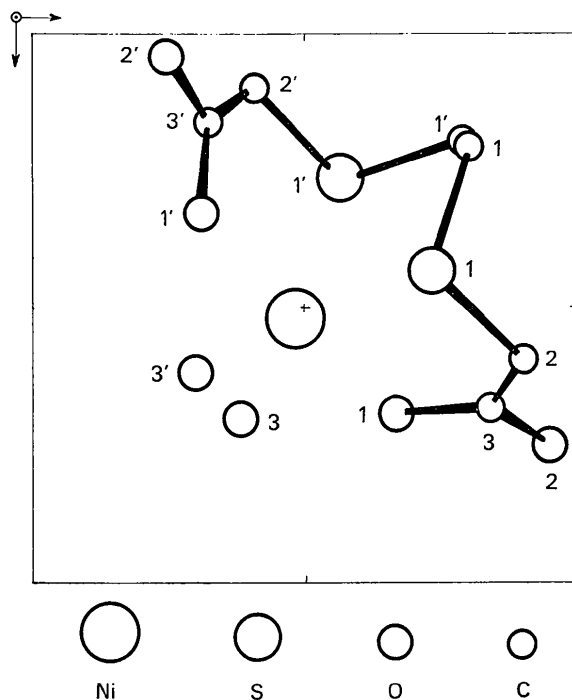


Fig. 1. Structure of nickel ethylenedithiodiacetate dihydrate viewed down z . The fractional coordinates of Ni are $x = 0.5228$, $y = 0.4772$, $z = 0.2500$.

square components of the atomic thermal vibration are presented.

The X-ray crystal structure determination of NEDDD have confirmed the indirect evidence concerning the arrangement around the nickel atom. Six atoms are octahedrally coordinated to nickel forming its first coordination sphere (Fig. 1). These are two *cis* sulphur atoms, two *cis* water molecules and two *trans* carboxylic oxygen atoms. The Ni-S distance of 2.44 Å in the compound studied is typical for a Ni → S bond and near to that in, e.g., nickel hexakis-(thiourea)bromide (Weininger, O'Connor & Amma, 1969) or nickel bisdiethyldithiophosphate bispyridinate (Ooi & Fernando, 1967). The distances Ni-O(1) (carboxylic) and Ni-O(3) (water) are 2.01 and 2.04 Å respectively and agree equally well with analogous Ni-O distances in other nickel carboxylates, e.g. in nickel dihydrogen ethylenediaminetetraacetate (Smith & Hoard, 1959) these distances were found to be 2.03 and 2.08 Å respectively.

The acetate 'arm' formed by C(2)C(3)O(1)O(2) adopts a nearly planar arrangement, the O(2) carbonyl oxygen distance from the C(2)C(3)O(1) plane being only 0.1 Å. It should be pointed out that this deviation from planarity is smaller than in related aminopolycarboxylate complexes. For comparison, the same distance in a molybdenum(VI) complex of ethylenediaminetetraacetic acid is 0.3 Å (Park, Glick & Hoard, 1969).

In the crystal framework, two of the numerous intermolecular O-O distances can be assumed to indicate the presence of medium-intensity hydrogen bonding: O(3)-O(2''), 2.693 ± 10 Å and O(3)-O(2''') 2.798 ± 10 Å. Fractional coordinates of atoms O(2'') and O(2''') are:

	x	y	z
O(2'')	1.0426	0.2478	0.3123
O(2''')	0.5426	0.2522	0.4377

The powder diagrams of the analogous cobalt and iron compounds, $\text{Co}(\text{CH}_2\text{SCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}(\text{CH}_2\text{SCH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Podlaha & Podlahová, 1971), have indicated that these compounds are isostructural with the nickel compound.

The authors are indebted to Dr M. Ebert from the Department of Inorganic Chemistry of Charles University for having made this work possible and to Dr A. Líněk from the Institute of Solid State Physics of Czechoslovak Academy of Sciences for helpful discussions.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS. A Fortran Crystallographic Least-squares Program*. Oak Ridge National Laboratory, Tennessee.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE, Fortran Crystallographic Function and Error Program*. Oak Ridge National Laboratory, Tennessee.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.

- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.
- HADINEC, I. (1969). Private communication.
- International Tables for X-ray Crystallography* (1962a). Vol II, Table 5.3.6.B. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962b). Vol III. Birmingham: Kynoch Press
- LOUB, J. & PODLAHOVÁ, J. (1971). *Inorg. Nucl. Chem. Letters*, **7**, 409.
- OOI, S. & FERNANDO, Q. (1967). *Inorg. Chem.* **6**, 1558.
- PARK, J. J., GLICK, M. D. & HOARD, J. L. (1969). *J. Amer. Chem. Soc.* **91**, 301.
- PODLAHA, J. & PODLAHOVÁ J. (1970). *Inorg. Chim. Acta*, **4**, 521.
- PODLAHA, J. & PODLAHOVÁ J. (1971). *Inorg. Chim. Acta*, **5**, 413.
- SMITH, D. L. (1969). *Acta Cryst.* **B25**, 628.
- SMITH, G. S. & HOARD, J. L. (1959). *J. Amer. Chem. Soc.* **81**, 556.
- WEININGER, M. S., O'CONNOR, J. E. & AMMA, E. L. (1969). *Inorg. Chem.* **8**, 424.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1972). **B28**, 1626

The Crystal Structure of the 'Normal Tetrahedral' Compound $\text{Cu}_2\text{CdSiS}_4$ *

G. CHAPUIS AND A. NIGGLI

Federal Institute of Technology, Department of Crystallography and Petrography, 8006 Zürich, Switzerland

(Received 1 November 1971)

The structure of $\text{Cu}_2\text{CdSiS}_4$ is a superstructure of the wurtzite type. Crystallizing in the space group $Pmn2_1$ with the lattice parameters $a = 7.60$ ($\approx 2a_{\text{wurtzite}}$), $b = 6.48$ ($\approx \sqrt{3}a_{\text{wurtzite}}$) and $c = 6.25$ Å ($\approx c_{\text{wurtzite}}$), the unit cell contains 2 formula units $\text{Cu}_2\text{CdSiS}_4$ (calculated density $D_x = 4.26$). The structure was postulated by geometrical considerations and by taking into account systematic and pseudo-selection rules; it was confirmed by Fourier syntheses. Half the tetrahedral voids of the hexagonal close sulphur packing are regularly occupied by two Cu, one Cd and one Si atom, while the coordination of the electropositive elements by sulphur is also tetrahedral. This structure is a 'normal tetrahedral' one, [after Parthé, E., *Crystal Chemistry of Tetrahedral Structures*, New York, Gordon & Breach (1964)], and represents a limiting member of the series wurtzite- $\text{Cu}_2\text{CdSiS}_4$, just as $\text{Cu}_2\text{FeSnS}_4$ does in the series sphalerite-stannite with cubic close sulphur packing.

Introduction

In a short communication (Chapuis & Niggli, 1968) the idealized structure of the new compound $\text{Cu}_2\text{CdSiS}_4$ has been described. Simultaneously and independently, Parthé, Yvon & Deitch (1969) solved the structure of an isomorphous compound $\text{Cu}_2\text{CdGeS}_4$. This structure type belongs to the 'tetrahedral structures' (Parthé, 1964) and may be described as a superstructure of the wurtzite type. $\text{Cu}_2\text{CdSiS}_4$ and $\text{Cu}_2\text{CdGeS}_4$ are the first tetrahedral quaternary compounds known with a hexagonal close-packing of sulphur atoms; the mineral stannite ($\text{Cu}_2\text{FeSnS}_4$) has a corresponding tetrahedral structure with a cubic close-packing of sulphur atoms.

Experimental

Crystal data

$\text{Cu}_2\text{CdSiS}_4$, formula weight: 395.8
Habit: prismatic c
 $a = 7.598$ (8), $b = 6.486$ (6), $c = 6.258$ (11) Å
 $V = 1978.5$ (1.4) Å³

$$Z = 2, D_x = 4.27 \text{ g.cm}^{-3}$$

$$\lambda_{\text{Mo K}\alpha} = 0.71069 \text{ Å}$$

$$\text{Selection rule for } h0l: h + l = 2n$$

Approximate pseudo-extinctions:

$$(h = 2n) \frac{1}{2}h + k = 2n, (h = 2n, k = 3n) \frac{1}{2}h + \frac{1}{3}k + l = 2n$$

Space group $Pmn2_1$

$$\mu_{\text{Mo}} = 117 \text{ cm}^{-1}$$

Crystal size of the specimen cut: $0.1 \times 0.1 \times 0.1$ mm.

The compound $\text{Cu}_2\text{CdSiS}_4$ has been synthesized by Nitsche, Sargent & Wild (1967) by transport reactions with iodine in the gas phase and a temperature gradient of 800 to 750°C. The crystal has been measured on a Picker automatic diffractometer (FACS 1). With an Ni filter (0.05 mm) in the diffracted beam and a maximal 2θ -value of 65°, 2440 reflexions hkl have been measured with a scintillation counter by the θ - 2θ scan method (scanning length: $2\theta = 1.2^\circ$, this value being corrected for the separation of the $K\alpha_1$ and $K\alpha_2$ lines). For each reflexion, the background has been measured on both sides of the peak. After correction of the Lorentz and polarization factors (no absorption correction), 642 independent reflexions have been obtained with the calculated weights $w = 1/\sigma^2(F) = (2F/\sigma_c)^2$ where σ_c = standard deviation of the observation (Poisson).

* This work is a part of the Ph.D. thesis of G. C.