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The Ethylammonium Salt of the Nickel(II) Complex of Ethyldithiophosphonic Acid

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Abstract. $Ni[S_2P(O)C_2H_5]_2^{2-}.2(C_2H_5NH_3)^+$, M_r = 431·22, monoclinic, $P2_1/n$ (systematic absences $h0l$, $h + l \neq 2n$, $0k0$, $k \neq 2n$), a = 9·946 (1), b = 13·408 (2), c = 14·823 (2) Å, β = 99·58 (1)°, Z = 4, D_c = 1·469, D_m = 1·462 g cm^{-3}, μ = 13·6 cm^{-1} [λ(Mo $K\alpha$) = 0·71069 Å]. The structure was refined to a final R value of 0·042 for 2110 reflections. The Ni coordination is approximately square planar. There is an unusually short Ni—S distance of 2·212 (2) Å.

Introduction. The ethylammonium salt of the Ni^{II} chelate of ethyldithiophosphonic acid was isolated in the form of purple needle-shaped crystals in the course of the synthesis of the two forms of the Ni^{II} chelates of diethyldithiophosphonic acid by the reaction of C_2H_5MgBr with P_2S_5 (Shetty, Jose & Fernando, 1968). A crystal 0·3 × 0·2 × 0·07 mm was mounted along the a axis. A Syntex four-circle computer-controlled diffractometer ($P2_1$) with a graphite monochromator (Mo $K\alpha$ radiation, λ = 0·71069 Å) and a pulse-height analyzer was used for the data collection. The cell constants were determined by a least-squares treatment of 15 reflections with 2θ values between 11 and 30°. The θ–2θ scan technique was employed at a scan rate varying from 2·0 to 29·3° min^{-1} in 2θ; the scan range was 2·0°. One-half of the total scan time was spent counting the background at each end of the scan range. 2559 reflections with 2θ < 50° were collected, and those 2110 reflections for which the net counts exceeded three times the corresponding standard deviation were considered to be observed. There were no significant variations in the three check reflections that were monitored after every 100 reflections. Standard deviations were calculated in the usual manner (Corfield, Doedens & Ibers, 1967) and a value of 0·04 was assigned to p, the empirical parameter. The net counts were corrected for Lorentz and polarization effects. The structure was solved with the direct-method program *MULTAN* (Germain, Main & Woolfson, 1970), with E's > 1·5. A full-matrix isotropic refinement of the structure was followed by anisotropic refinement to an R_1 index [$= (\sum|F_o - |F_c||)/\sum F_o$] of 0·052. At this stage, most of the H atoms were located on a difference map and the positions of the rest were calculated. The H atoms were included in the refinement and the structure was refined to R_1 = 0·042 and the R_2 index $\{= [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}\}$ was 0·053. The refinement was based on F_o and the quantity minimized was $\sum w(F_o - |F_c|)^2$. The scattering factors used were those of Hanson, Herman, Lea &

Table 1. *Atomic positional parameters* (×10^4)

	x	y	z
Ni	4903 (1)	7919 (1)	2178 (1)
S(1)	6657 (2)	6866 (1)	2422 (1)
S(2)	3659 (2)	6729 (2)	2665 (1)
P(1)	5379 (2)	5895 (2)	2902 (1)
O(1)	5797 (5)	5597 (4)	3906 (3)
N(1)	3474 (6)	6030 (5)	4951 (4)
C(1)	5176 (8)	4765 (6)	2228 (5)
C(2)	4739 (12)	4914 (8)	1210 (6)
C(3)	3586 (9)	7009 (7)	5433 (6)
C(4)	2886 (12)	7814 (8)	4888 (8)
S(2')	6161 (2)	9135 (1)	1732 (1)
S(1')	3121 (2)	8957 (2)	1881 (1)
P(1')	4541 (2)	10032 (2)	1795 (1)
O(1')	4210 (5)	10745 (4)	999 (3)
N(1')	6476 (6)	11464 (5)	316 (4)
C(1')	4811 (8)	10769 (6)	2837 (5)
C(2')	4993 (12)	10151 (9)	3717 (6)
C(3')	6363 (9)	12561 (7)	356 (6)
C(4')	7597 (11)	13054 (8)	146 (8)
H1(C1)	4504	4341	2440
H2(C1)	6018	4397	2321
H1(C2)	3800	5100	1080
H2(C2)	4869	4332	865
H3(C2)	5262	5445	997
H1(N1)	3993	5587	5272
H2(N1)	3719	6083	4418
H3(N1)	2627	5807	4872
H1(C3)	4523	7191	5583
H2(C3)	3221	6957	5987
H1(C4)	3000	8500	5140
H2(C4)	1913	7681	4800
H3(C4)	3149	7822	4303
H1(C1')	4058	11221	2842
H2(C1')	5615	11185	2852
H1(C2')	4999	10548	4253
H2(C2')	5837	9789	3787
H3(C2')	4271	9676	3685
H1(N1')	7250	11258	628
H2(N1')	5800	11200	540
H3(N1')	6439	11258	−253
H1(C3')	6218	12761	952
H2(C3')	5579	12782	−72
H1(C4')	7600	13767	130
H2(C4')	7748	12837	−455
H3(C4')	8369	12847	573

Skillman (1964). Corrections were made for the anomalous dispersion of Ni, S and P atoms. The values used were $f' = 0{\cdot}37$, $f'' = 1{\cdot}10$ for Ni; $f' = 0{\cdot}10$, $f'' = 0{\cdot}20$ for S; and $f' = 0{\cdot}11$, $f'' = 0{\cdot}12$ for P.*

Discussion. The final positional parameters of the atoms are given in Table 1. The bond lengths and bond angles (together with their standard deviations in parentheses) are collected in Table 2. Fig. 1 shows an *ORTEP* (Johnson, 1965) drawing of the chelate and the ethylammonium ion. The coordination around the Ni atom is approximately square planar. The angle between the least-squares planes through Ni, S(1), S(2), P(1) and Ni, S(1′), S(2′), P(1′) is 9·95°. The deviations of P(1) and P(1′) from the least-squares plane through S(1), S(1′), S(2) and S(2′) are −0·085 and −0·430 Å respectively. The intramolecular hydrogen bonds are N(1)···O(1) 3·004, and N(1′)···O(1′) 2·792 Å. The intermolecular hydrogen bonds are N(1)···O(1)-$[1-x,\ 1-y,\ 1-z]$ 2·783, N(1)···O(1′)$[\frac{1}{2}-x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z]$ 2·829, and N(1′)···O(1′)$[\frac{3}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z]$ 3·000 Å. There is a short intermolecular contact of 3·394 Å between N(1′)$[x,y,z]$ and S(2′)$[1-x,\ 2-y,\ -z]$. The N—H···O bond angles around N(1′) are close to 180°, whereas they are 120, 140 and 130° around N(1). Fig. 2 shows the packing of the ions in the unit cell. The distances Ni—S(1) (2·226 Å), Ni—S(1′) (2·239 Å) and Ni—S(2′) (2·221 Å) are within the range of values found for low-spin Ni complexes (Shetty & Fernando, 1969; Wasson, Woltermann & Stoklosa, 1973). The Ni—S(2) distance (2·212 Å), however, is unusually short. The average P—S distance of 2·029 (2) Å is about the same as the P—S distances found in the bis(*O,O′*-diethyldithiophosphato)nickel(II) complex

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33674 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°) *involving non-hydrogen atoms*

Ni—S(1)	2·226 (2)	S(1)—Ni—S(2)	87·4 (1)
Ni—S(2′)	2·221 (2)	S(1)—Ni—S(2′)	92·8 (1)
Ni—S(2)	2·212 (2)	S(1)—Ni—S(1′)	178·0 (1)
Ni—S(1′)	2·239 (2)	S(2′)—Ni—S(1′)	87·2 (1)
S(1)—P(1)	2·029 (3)	S(2)—Ni—S(2′)	178·2 (1)
S(2)—P(1)	2·025 (3)	S(2)—Ni—S(1′)	92·6 (1)
S(2′)—P(1′)	2·025 (3)	Ni—S(1)—P(1)	86·8 (1)
S(1′)—P(1′)	2·036 (3)	Ni—S(2)—P(1)	87·3 (1)
P(1)—O(1)	1·530 (5)	Ni—S(2′)—P(1′)	86·0 (1)
P(1′)—O(1′)	1·512 (5)	Ni—S(1′)—P(1′)	85·3 (1)
P(1)—C(1)	1·807 (8)	S(1)—P(1)—S(2)	98·3 (1)
P(1′)—C(1′)	1·816 (8)	S(2)—P(1)—O(1)	115·1 (2)
C(1)—C(2)	1·513 (11)	S(1)—P(1)—C(1)	111·3 (3)
C(1′)—C(2′)	1·531 (11)	S(2)—P(1)—O(1)	113·4 (2)
N(1)—C(3)	1·489 (10)	S(2)—P(1)—C(1)	110·7 (3)
N(1′)—C(3′)	1·476 (11)	O(1)—P(1)—C(1)	107·8 (3)
C(3)—C(4)	1·456 (14)	S(2′)—P(1′)—S(1′)	98·5 (2)
C(2′)—C(4′)	1·472 (14)	S(2′)—P(1′)—O(1′)	114·3 (3)
		S(2′)—P(1′)—C(1′)	110·9 (3)
		S(1′)—P(1′)—O(1′)	115·7 (2)
		S(1′)—P(1′)—C(1′)	109·8 (3)
		O(1′)—P(1′)—C(1′)	107·5 (3)
		P(1)—C(1)—C(2)	115·4 (6)
		P(1′)—C(1′)—C(2′)	114·2 (6)
		N(1)—C(3)—C(4)	113·4 (7)
		N(1′)—C(3′)—C(4′)	111·5 (7)

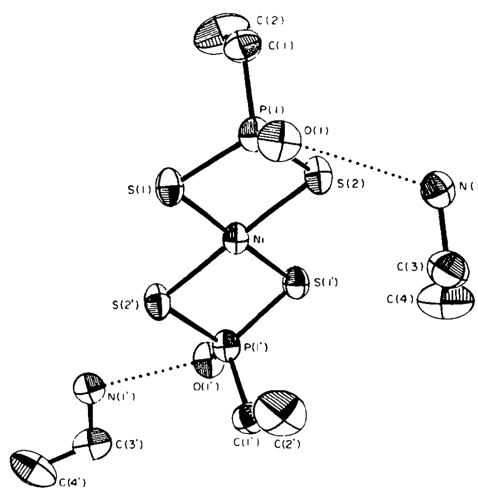

Fig. 1. The molecular configuration of $Ni[S_2P(O)C_2H_5]_2^{2-}.2(C_2H_5NH_3)^+$.

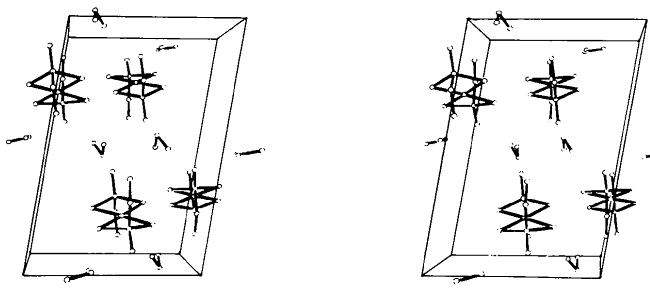

Fig. 2. Molecular packing in the unit cell.

(1·986–1·993 Å), and in the bis(diethyldithiophosphinato)nickel(II) complex (2·00–2·01 Å) (McConnell & Kastalsky, 1967; Shetty & Fernando, 1969). The bonding of the P atom to a C atom of an ethyl group and to an O atom with a partial negative charge is reflected in the longer P—S bond in this unsymmetrically substituted complex. The P—C and C—C distances are close to the normal values. As expected, the P—O distance of 1·521 (5) Å is significantly shorter than the corresponding P—O distances in complexes of the type $Ni[S_2P(OR)_2]_2$ (Wasson, Woltermann & Stoklosa, 1973). The C—N distance in the ethylammonium ion is close to the normal value, but the C—C distance is about 0·06 Å shorter than the corresponding distance in ethylammonium tetrachloromanganate(II) (Depmeier, 1975).

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Magnesium Bis(hydrogen malonate) Dihydrate

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Abstract. $Mg(C_3H_3O_4)_2.2H_2O$, $M_r = 266·5$, monoclinic, $P2_1/c$, $a = 4·9391$ (5), $b = 11·3100$ (13), $c = 9·6497$ (9) Å and $\beta = 90·312$ (7)°, $V = 539·0$ Å^3, $Z = 2$, $R = 0·038$. The compound consists of hydrogen malonate chains crosslinked by the Mg^{2+} ion. The Mg ion is surrounded by two water molecules and four carboxylate O atoms forming a slightly distorted octahedron. The short (2·589 Å) hydrogen bond in the hydrogen malonate chain is probably asymmetric.

Introduction. Crystals of $Mg(C_3H_3O_4)_2.2H_2O$ were obtained by evaporation of an aqueous solution of magnesium hydrogen malonate. Weissenberg photographs showed that the compound is monoclinic; systematic absences $0k0$ with $k \neq 2n$ and $h0l$ with $l \neq 2n$ uniquely define the space group as $P2_1/c$. Accurate cell dimensions were obtained by a least-squares treatment of powder spectra recorded with a Guinier–Hägg focusing camera (Cu $K\alpha_1$ radiation, $\lambda = 1·54056$ Å, 22 °C). Aluminium (cubic, $a = 4·04934$ Å) was used as internal standard. A four-circle single-crystal diffractometer (CAD-4) was used in the intensity data collection. Experimental conditions and data reduction are described by Oskarsson (1978). Some specific experimental parameters and information concerning the least-squares refinement are given in Table 1. The positions of the non-H atoms were determined by symbolic addition (Karle & Karle, 1963, 1966). Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ was performed with weights $w^{-1} = \sigma_c^2(|F_o|^2)/4|F_o|^2 + C|F_o|^2$. $\sigma_c(|F_o|^2)$ is estimated from counting statistics. C was adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2\rangle$ were obtained in different $|F_o|$ and $\sin\theta$ intervals. The H atoms were located in a difference synthesis using data corrected for isotropic extinction (Zachariasen, 1967) and obeying $\sin\theta/\lambda < 0·5$ Å^{-1}. In the last cycle of refinement, the shifts in the parameters were less than 10% of the e.s.d.'s. Atomic

Table 1. *Summary of data collection and least-squares refinement*

Crystal size: 0·282 × 0·150 × 0·140 mm
$\lambda = 0·7107$ Å (graphite-monochromated Mo $K\alpha$)
$\mu = 2·4$ cm^{-1}
Range of transmission factor: 0·95–0·97
θ interval: 3–30°
ω–2θ scan width $\Delta\omega = 0·7 + 0·5 \tan\theta$ (°)
Minimum number of counts in a scan: 3000
Maximum recording time: 3 min
Number of measured reflexions: 1612
Number of reflections with zero weight ($I \leq 0$): 74
Number of parameters refined: 100
$R = \sum ||F_o| - |F_c||/\sum |F_o| = 0·038$
$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0·40$
$S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2} = 1·6$
C (weighting function): 0·015
$g \times 10^4 = 0·11$ (5) (extinction)