Dithiocarbimates from Sulfonamides, Part 2: Preparation and X-Ray Crystal Structures of $(PPh_4)_2[Ni(S_2C{=}N{-}SO_2{-}Ph)_2]$ and $(PPh_4)_2[Ni(S_2C{=}N{-}SO_2{-}C_6H_4{-}Cl)_2]\cdot 2\,H_2O$

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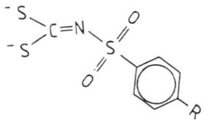
Nickel(II), N-Sulfonyldithiocarbimates, X-Ray

By reaction of $K_2[S_2CNSO_2C_6H_5]\cdot 2\,H_2O$ and $K_2[S_2CNSO_2C_6H_4Cl]\cdot 2\,H_2O$, respectively, with $Ni(CH_3COO)_2\cdot 4\,H_2O$ the complex anions $[Ni(S_2C{=}N{-}SO_2{-}C_6H_5)_2]^{2-}$ and $[Ni(S_2C{=}N{-}SO_2{-}C_6H_4{-}Cl)_2]^{2-}$ are formed and have been isolated in form of their (PPh_4) salts. $(PPh_4)_2[Ni(S_2C{=}N{-}SO_2{-}Ph)_2]$ crystallizes monoclinicly, space group $P2_1/a$ with $a = 19.081(4)$, $b = 9.106(1)$, $c = 17.630(4)$ Å and $\beta = 113.42(6)°$ with $Z = 2$. $(PPh_4)_2[Ni(S_2C{=}N{-}SO_2{-}C_6H_4{-}Cl)_2]\cdot 2\,H_2O$ crystallizes triclinicly, and the non-standard setting $C\bar{1}$ has been choosen with $a = 15.732(3)$, $b = 22.509(4)$, $c = 9.521(1)$ Å, $\alpha = 96.30(6)$, $\beta = 117.57(9)$, $\gamma = 88.93(5)°$ and $Z = 2$. Within the complex anions nickel has the site-symmetry $\bar{1}$ and is coordinated by four sulfur atoms with Ni–S mean = 2.198 Å. The $Ni(S_2C{=}N{-}SO)_2$ units are essentially planar in both systems. This planarity gives rise to conjugation effects involving the SO_2 group and the π-system of $S_2C{=}N-$ as well as the lone pair on N.

Introduction

Dithiocarbamates of nickel(II) have been well known for a long time, and numerous complexes having the general formula $Ni(RR'NCS_2)_2$ have been synthesized and characterized [1, 2]. Nevertheless only few complexes $(cat)_2(NiL_2)$ with related binegative ligands (*i.e.* L = 1,1-disubstituted ethylene-2,2-dithiolate, trithiocarbonate or dithiocarbimate) have been described [3–5]. In fact the only structurally characterized species that contains a dithiocarbimate ligand is $(AsPh_4)_2[Ni(S_2C{=}N{-}CN)_2]$ [5]. Hence there is considerable lack of information concerning structural properties and reactivity of nickel complexes with dithiocarbimates. In a previous paper we have reported on the preparation and structures of the potassium salts of N-sulfonyldithiocarbimates **1** and **2** (see below) [6], while in the present publication we describe the preparation and X-ray structural analysis of $(PPh_4)_2[Ni(\mathbf{1})_2]$ and $(PPh_4)[Ni(\mathbf{2})_2]\cdot 2\,H_2O$.



R = H: **1**
R = Cl: **2**
R = CH_3: **3**
R = NO_2: **4**

Experimental

Preparation of $(PPh_4)_2[Ni(\mathbf{1})_2]$ and $(PPh_4)_2[Ni(\mathbf{2})_2]\cdot 2\,H_2O$

The complexes have been synthesized from stoichiometric amounts of $K_2\mathbf{1}\cdot 2\,H_2O$ and $K_2\mathbf{2}\cdot 2\,H_2O$, respectively, with $Ni(CH_3COO)_2\cdot 4\,H_2O$ in H_2O. On addition of $(PPh_4)Br$ in H_2O/acetone, yellow-green precipitates of the title compounds have been obtained. The products can be recrystallized from CH_3CN.

	C	H	N	S	decomp. (K)
$(PPh_4)_2[Ni(\mathbf{1})_2]$	62.05	4.20	2.33	16.03	484
Calcd (%)	62.27	4.05	2.23	16.19	
Found (%)					
$(PPh_4)_2[Ni(\mathbf{2})_2]\cdot 2H_2O$					490
Calcd (%)	57.01	3.98	2.14	14.71	
Found (%)	58.64	3.90	2.13	14.39	

X-ray structure analysis

The process of X-ray structure analysis of the title compounds is similar to that described elsewhere [6] and needs not to be given in detail. The crystal data of $(PPh_4)_2[Ni(\mathbf{1})_2]$ and $(PPh_4)_2[Ni(\mathbf{2})_2]\cdot 2\,H_2O$ have been collected in Table I, Tables II and III contain atomic coordinates and temperature factors of the non-hydrogen atoms of the title compounds.

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Table I. Crystallographic details for the X-ray structure determinations of $(PPh_4)_2[Ni(\mathbf{1})_2]$ and $(PPh_4)_2[Ni(\mathbf{2})_2] \cdot 2\,H_2O$*.

Formula	$(PPh_4)_2[Ni(S_2C{=}N{-}SO_2{-}C_6H_5)_2]$	$(PPh_4)_2[Ni(S_2C{=}N{-}SO_2{-}C_6H_4{-}Cl)_2] \cdot 2\,H_2O$
M_r	1200.14	1303.08
a [Å]	19.081(4)	15.732(3)
b [Å]	9.106(1)	22.509(4)
c [Å]	17.630(4)	9.521(1)
α [°]	90.0	96.30(6)
β [°]	113.42(6)	117.57(9)
γ [°]	90.0	88.93(5)
V [Å^3]	2810.88	2968.65
Z	2	2
d_x [g cm^{-3}]	1.42	1.46
Space group	$P2_1/a$ No. 14 [15]	$C\bar{1}$**
Diffractometer	HUBER	PHILIPS
λ [Å]	MoK_α −0.70926	AgK_α −0.55970
Temp. [K]	293±2	293±2
θ-range [°]	$3 \leq \theta \leq 25$	$2 \leq \theta \leq 20$
Total reflections	4902	11148
Symmetry-independent reflections	2553	4971
Observed reflections	1259 $F_o \geq 6\sigma(F)$	2545 $F_o \geq 5\sigma(F)$
Structure solution	direct methods, SHELXS-86	direct methods, SHELXS-86 [16]
Refinement	SHELX-76 Anisotropically: Ni, S1, S2, S3, C1, N, O1, O2, P	SHELX-76 [17] Anisotropically: Ni, S1, S2, S3, Cl, P
	Phenylgroups: riding model with geometrically fixed protons	
Number of parameters	141	134
R	0.079	0.061
R_w	0.078	0.072

* Additional crystal structure data have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Inquieries should be accompanied by the depository number CSD 53410, the names of the authors, and the literature citation.

** For $(PPh_4)_2[Ni(\mathbf{2})_2] \cdot 2\,H_2O$ a C-centred triclinic lattice has been choosen for better comparison to $(PPh_4)_2[Ni(\mathbf{1})_2]$. The standard setting is P1 with $a = 9.521(1)$, $b = 13.610(3)$, $c = 13.771(3)$ Å, $\alpha = 62.11(5)$, $\beta = 70.29(5)$, $\gamma = 79.82(6)°$ and $Z = 1$.

Table II. Atomic coordinates and temperaturefactors for the non-hydrogen atoms of $(PPh_4)_2[Ni(\mathbf{1})_2]$.
$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ (Å^2).

Atom	x	y	z	U_{eq} or U_{iso}*
Ni	0.0	0.0	0.5	0.1269(54)
S1	0.0439(2)	0.1655(5)	0.4399(3)	0.1411(77)
S2	0.0336(2)	0.8624(5)	0.4169(2)	0.1352(77)
S3	0.0653(2)	0.1811(5)	0.2623(3)	0.1168(79)
O1	0.9914(5)	0.2509(12)	0.2344(6)	0.148(12)
O2	0.0918(6)	0.1399(12)	0.1995(6)	0.161(12)
C1	0.0514(8)	0.0259(15)	0.3795(9)	0.106(13)
N	0.0670(7)	0.0312(13)	0.3128(8)	0.133(13)
C21	0.1320(5)	0.3042(8)	0.3288(5)	0.0876(31)*
C22	0.2157(5)	0.2544(8)	0.2763(5)	0.0993(32)*
C23	0.2615(5)	0.3530(8)	0.4247(5)	0.1055(33)*
C24	0.2436(5)	0.5014(8)	0.4256(5)	0.1043(32)*
C25	0.1700(5)	0.5512(8)	0.3780(5)	0.1203(35)*
C26	0.1142(5)	0.4526(8)	0.3296(5)	0.0970(32)*
P	0.3121(2)	0.7765(5)	0.1746(2)	0.1279(72)
C31	0.1783(4)	0.9394(8)	0.1085(4)	0.0833(30)*
C32	0.1104(4)	0.9810(8)	0.0441(4)	0.1003(32)*
C33	0.0942(4)	0.3926(8)	0.9638(4)	0.0988(32)*
C34	0.1459(4)	0.8425(8)	0.9479(4)	0.0872(31)*
C35	0.2139(4)	0.8008(8)	0.0124(4)	0.0924(31)*
C36	0.2301(4)	0.8493(8)	0.0927(4)	0.0812(30)*
C41	0.3938(4)	0.9306(8)	0.1039(5)	0.1058(33)*
C42	0.4588(4)	0.9635(8)	0.0894(5)	0.1186(35)*
C43	0.5222(4)	0.8709(8)	0.1195(5)	0.1117(34)*
C44	0.5206(4)	0.7454(8)	0.1642(5)	0.1112(34)*
C45	0.4556(4)	0.7124(8)	0.1787(5)	0.0934(32)*
C46	0.3922(4)	0.8051(8)	0.1485(5)	0.0828(30)*
C51	0.2289(4)	0.5180(8)	0.1347(4)	0.0896(31)*
C52	0.2154(4)	0.3723(8)	0.1495(4)	0.1058(33)*
C53	0.2679(4)	0.2979(8)	0.2175(4)	0.1094(34)*
C54	0.3339(4)	0.3691(8)	0.2707(4)	0.1063(33)*
C55	0.3473(4)	0.5147(8)	0.2559(4)	0.0924(31)*
C56	0.2948(4)	0.5891(8)	0.1879(4)	0.0768(29)*
C61	0.2866(4)	0.8269(8)	0.3150(5)	0.0960(32)*
C62	0.3039(4)	0.8862(8)	0.3934(5)	0.1116(34)*
C63	0.3650(4)	0.9834(8)	0.4274(5)	0.1037(33)*
C64	0.4089(4)	0.0211(8)	0.3631(5)	0.1037(33)*
C65	0.3916(4)	0.9613(8)	0.3048(5)	0.0919(32)*
C66	0.3304(4)	0.8647(8)	0.2707(5)	0.0770(29)*

Table III. Atomic coordinates and temperaturefactors for the non-hydrogen atoms of $(PPh_4)_2[Ni(\mathbf{2})_2] \cdot 2\,H_2O$.

Atom	*x*	*y*	*z*	U_{eq} or U_{iso}*
Ni	0.0	0.5	0.5	0.0639(20)
S1	0.1147(1)	0.4377(1)	0.5344(2)	0.1136(31)
S2	0.9668(1)	0.4314(1)	0.6177(2)	0.1000(30)
C1	0.0702(4)	0.3985(3)	0.6334(7)	0.0416(13)*
N	0.1027(3)	0.3523(2)	0.7154(6)	0.0447(11)*
S3	0.2030(1)	0.3225(1)	0.7444(2)	0.1024(31)
O1	0.2215(3)	0.3195(2)	0.6088(6)	0.0671(12)*
O2	0.2032(3)	0.2666(2)	0.8049(6)	0.0693(12)*
C21	0.2909(2)	0.3702(1)	0.8993(4)	0.0439(13)*
C22	0.3149(2)	0.3638(1)	1.0573(4)	0.0581(14)*
C23	0.3768(2)	0.4058(1)	1.1799(4)	0.0645(15)*
C24	0.4148(2)	0.4542(1)	1.1446(4)	0.0620(15)*
C25	0.3908(2)	0.4605(1)	0.9867(4)	0.0684(15)*
C26	0.3289(2)	0.4285(1)	0.8640(4)	0.0609(15)*
Cl	0.4909(2)	0.5067(1)	0.2937(3)	0.1033(40)
P	0.7230(1)	0.1302(1)	0.0895(2)	0.0513(27)
C31	0.6081(2)	0.1618(1)	0.9875(4)	0.0359(12)*
C32	0.5497(2)	0.1676(1)	0.0622(4)	0.0484(13)*
C33	0.4607(2)	0.1935(1)	0.9880(4)	0.0556(14)*
C34	0.4300(2)	0.2137(1)	0.8392(4)	0.0607(15)*
C35	0.4885(2)	0.2079(1)	0.7646(4)	0.0589(14)*
C36	0.5775(2)	0.1820(1)	0.8387(4)	0.0505(14)*
C41	0.7034(2)	0.0594(1)	0.1415(4)	0.0384(12)*
C42	0.7566(2)	0.0431(1)	0.2951(4)	0.0456(13)*
C43	0.7397(2)	0.9872(1)	0.3299(4)	0.0562(14)*
C44	0.6696(2)	0.9477(1)	0.2112(4)	0.0581(14)*
C45	0.6165(2)	0.9640(1)	0.0576(4)	0.0611(15)*
C46	0.6334(2)	0.0199(1)	0.0228(4)	0.0551(14)*
C51	0.7799(2)	0.1216(2)	0.9625(4)	0.0385(13)*
C52	0.7381(2)	0.0827(2)	0.8216(4)	0.0528(14)*
C53	0.7796(2)	0.0771(2)	0.7197(4)	0.0602(15)*
C54	0.8632(2)	0.1104(2)	0.7586(4)	0.0531(14)*
C55	0.9049(2)	0.1493(2)	0.8996(4)	0.0616(15)*
C56	0.8633(2)	0.1549(2)	0.0015(4)	0.0532(14)*
C61	0.7984(2)	0.1792(1)	0.2644(4)	0.0387(12)*
C62	0.7656(2)	0.2343(1)	0.2978(4)	0.0457(13)*
C63	0.8254(2)	0.2729(1)	0.4319(4)	0.0566(14)*
C64	0.9181(2)	0.2565(1)	0.5325(4)	0.0578(14)*
C65	0.9510(2)	0.2014(1)	0.4991(4)	0.0619(15)*
C66	0.8911(2)	0.1628(1)	0.3651(4)	0.0460(14)*
O(W)	0.1701(5)	0.1594(3)	0.5543(8)	0.1146(15)*

Table IV. Selected distances and angles within the crystal structures of $(PPh_4)_2[Ni(\mathbf{1})_2]$ and $(PPh_4)[Ni(\mathbf{2})_2] \cdot 2\,H_2O$ in Å and degrees with esd's in parenthesis.

	$[Ni(\mathbf{1})_2]^{2-}$	$[Ni(\mathbf{2})_2]^{2-}$
Ni–S1	2.191(4)	2.188(2)
Ni–S2	2.208(4)	2.206(2)
S1···S2	2.785(6)	2.794(1)
S1–C1	1.70(1)	1.724(5)
S2–C1	1.72(1)	1.724(4)
C1–N	1.32(2)	1.320(7)
N–S3	1.62(1)	1.617(3)
S3–O1	1.44(1)	1.444(4)
S3–O2	1.44(1)	1.440(5)
S3–C21	1.751(9)	1.749(3)
Cl–C24	–	1.719(4)
S1–Ni–S2	78.6(2)	78.98(5)
C1–S1–Ni	86.1(5)	86.5(2)
C1–S2–Ni	85.2(5)	85.9(2)
S1–C1–S2	109.2(7)	108.3(3)
S1–C1–N	129.3(9)	131.7(3)
S2–C1–N	121.5(9)	120.0(3)
C1–N–S3	123.8(9)	122.2(3)
N–S3–C21	108.7(6)	104.5(2)
N–S3–O1	111.2(5)	114.5(3)
N–S3–O2	105.5(6)	105.7(2)
O1–S3–O2	116.6(6)	116.1(3)
O2–S3–C21–C22	−65.5(1)	−28.5(1)
Mean deviation from l.s. plane*	0.156(5)	0.079(5)

* The least-squares planes in each complex are defined through the atoms Ni, ±S1, ±S2, ±S3, ±C1, ±N, ±O2 where "+" and "−" denote atoms correlated by a centre of symmetry.

Discussion

Characteristic views of $[Ni(\mathbf{1})_2]^{2-}$ and $[Ni(\mathbf{2})_2]^{2-}$ are depicted in Figs. 1 and 2. The complex anions are very similar, and the NiS_4 group in both species is rigorously planar owing to the fact that the Ni atom lies at a crystallographic centre of symmetry (Tab. II and III).

Only small deviations from planarity are noted when the complete $Ni(S_2C{=}N{-}SO)_2$ fragments are considered and probably are due to packing forces. The Ni–S bond lengths correspond to usually observed values [1, 5, 7].

The conformation of complexed **1** and **2** exhibit characteristic alterations compared to that in the potassium salts [6]. The reduced S1–C1–S2 angles parallel decreased S1···S2 distances and are due to coordination effects. The binding of **1** and **2** to nickel results in nearly equal S1–C1 and S2–C1 bond lengths, but the values are unusually short and show some double-bond character [8]. The observed C1–N bond lengths are identical in both complexes and are close to the value of 1.287 Å, characteristic for C=N bonds (C–N: 1.472 Å) [9].

One of the most interesting features concerning the molecular geometry of **1** and **2** is the planar arrangement of the framework $S_2C{=}N{-}S{-}O$ [6]. This leads to a "cross conjugation" involving the SO_2 group and the π-system of S_2CN (case II of conjugation) as well as the lone-pair on $N_{sp}2$ (case I of conjugation) [10].

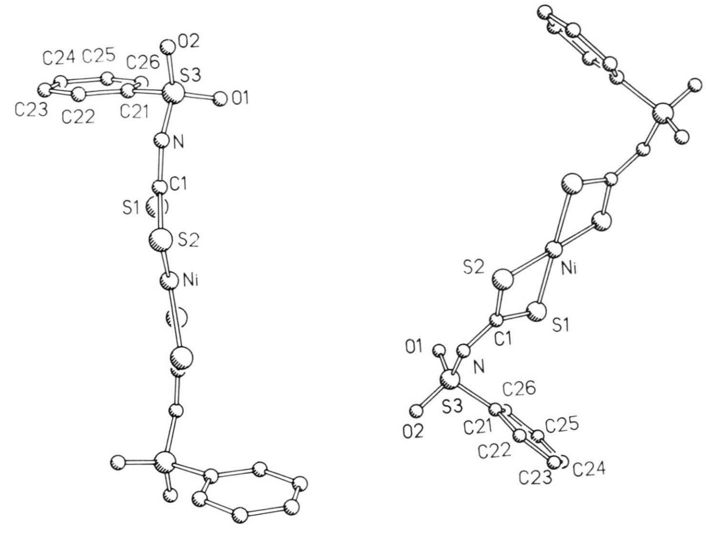


Fig. 1. Different views of the complex anion $[Ni(\mathbf{1})_2]^{2-}$. Ni(II) has the site-symmetry $\bar{1}$.

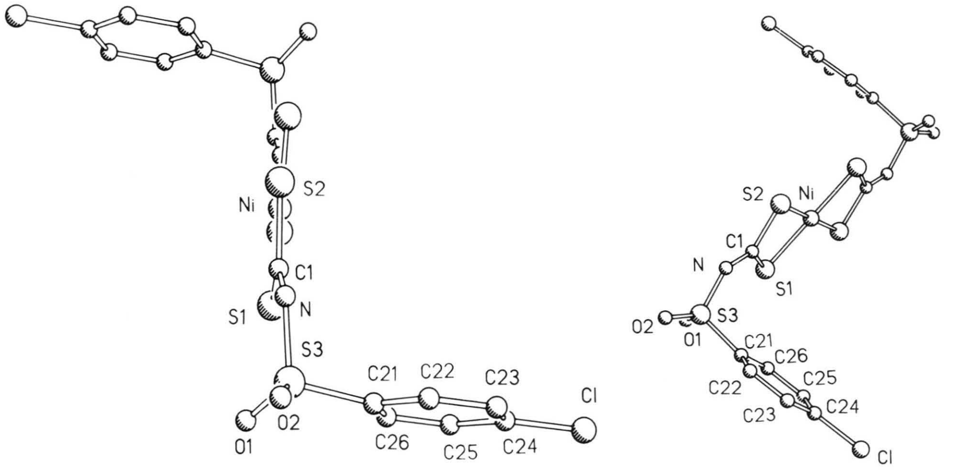
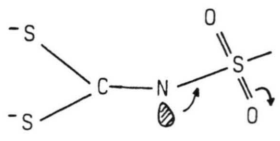


Fig. 2. The complex anion $[Ni(\mathbf{2})_2]^{2-}$ from different points of view. Ni(II) occupies a crystallographic centre of symmetry.

This arrangement in **1** and **2** is not altered when the ligands are associated with Ni(II), and the metal is incorporated into this system.

In Figs. 3 and 4 the unit cells of $(PPh_4)_2[Ni(\mathbf{1})_2]$ and $(PPh_4)_2[Ni(\mathbf{2})_2] \cdot 2\,H_2O$ are depicted. The tetraphenylphosphonium ions are only drawn schematically. Within this cations no unusual bond lengths and angles are observed (P–C mean = 1.787(7) Å) [11, 12]. From Fig. 4 it is obvious that the crystal water in $(PPh_4)_2[Ni(\mathbf{2})_2] \cdot 2\,H_2O$ is close to $-SO_2-$ of **2** (O(W)–O1 = 2.862(6), O(W)–O2 = 3.069(8) Å). While a value of 2.86 Å is regarded as a significant indication for hydrogen-bridging, the O(W)–O2 contact is on the upper limit of usually observed values [13, 14].



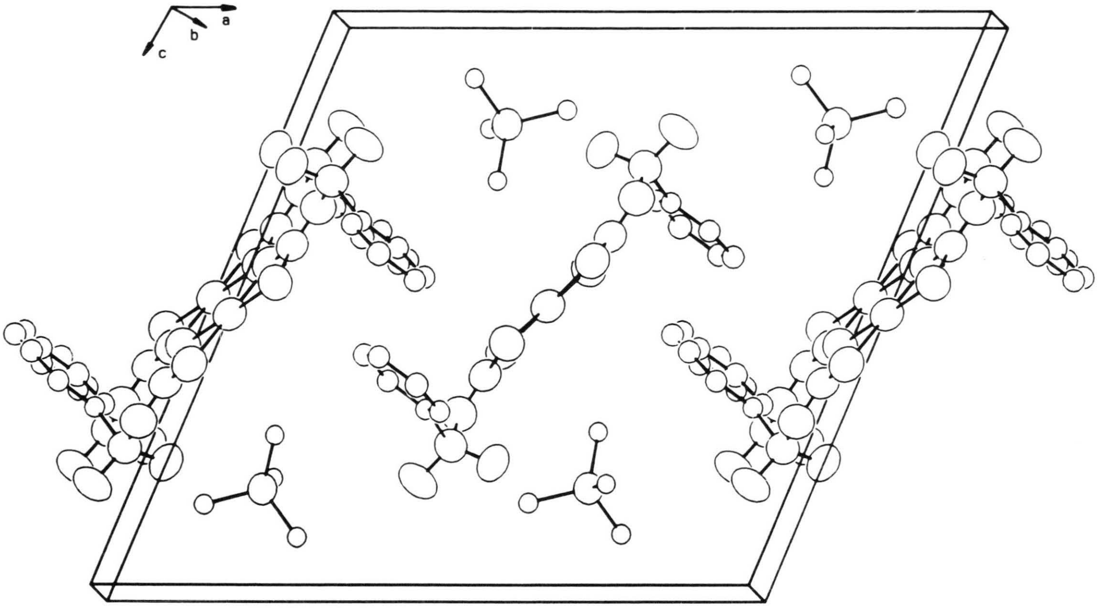


Fig. 3. The crystallographic unit cell of $(PPh_4)_2[Ni(\mathbf{1})_2]$. The tetraphenylphosphonium cations are schematic presented.

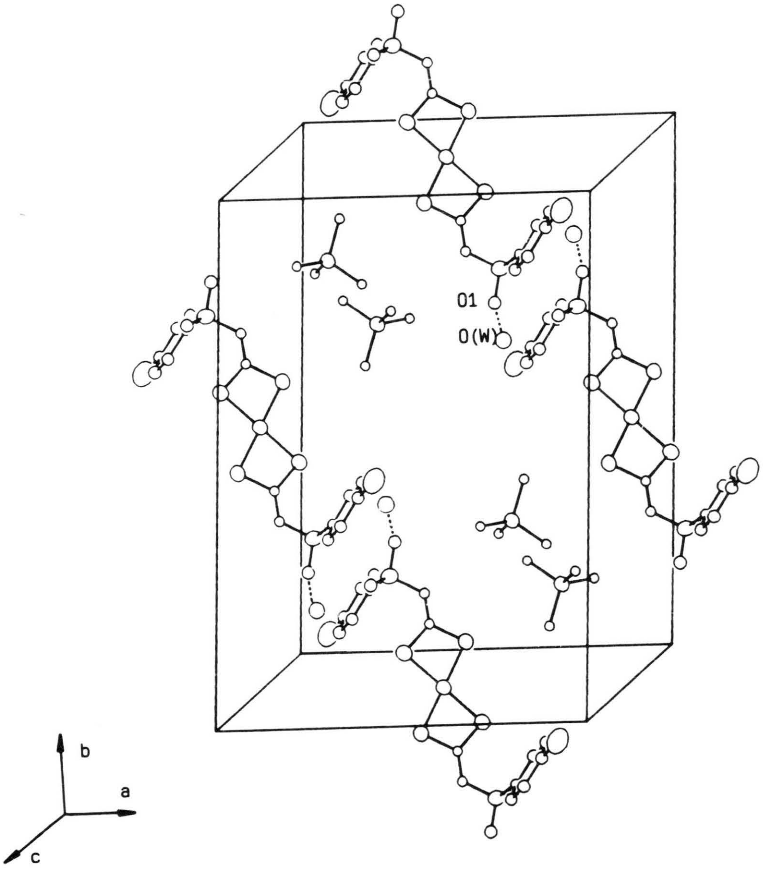


Fig. 4. The crystallographic unit cell of $(PPh_4)_2[Ni(\mathbf{2})_2] \cdot 2\,H_2O$. The contact between O(W) and O1 is indicated and the bulk PPh_4 group has been represented by tetrahedra.

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