The structure projected along the *b* axis is shown in Fig. 2. The complex anions are connected through the K^+ cations and the molecules of water of crystallization, forming infinite chains parallel to the *c* axis. The chains are held together by van der Waals forces only. The parameters of the hydrogen bonds formed within the chains are given in Table 3. No H atom attached to O(12) of the water molecule was found in the difference synthesis but from the O(12)···O(4) distance (Table 3) this hydrogen bond is also clearly indicated. The K^+ ion is seven-coordinated to five carboxylic oxygens of three different complex ions: O(1), O(5), O(2) $(-x, y, \frac{1}{2}-z)$, O(5) $(-x, 1-y, -z)$ and O(8) $(-x, -y, -z)$ and to two water molecules O(11) and O(12). The KO_7 polyhedron most closely approximates a monocapped tetragonal bipyramid; the atom O(1) is 'capped' over the face O(5), O(8) and O(12). The $K^+{\cdots}O$ distances range from 2·68 (1) to 3·07 (1) Å, mean 2·83 (1) Å, which corresponds to the sum of the ionic radius of K^+ for coordination number 7 (1·46 Å; Shannon & Prewitt, 1969) and the van der Waals radius of O (1·40 Å).

Table 3. *Hydrogen-bond parameters*

$A-H\cdots B$	$A-H$	$A\cdots B$	$H\cdots B$	Angle $H-A\cdots B$
$O(9)-H(O9)\cdots O(7^{ii})$	0·9 (1) Å	2·86 (1) Å	2·1 (1) Å	20 (8)°
$O(9)-H'(O9)\cdots O(6^{iii})$	0·9 (1)	2·85 (1)	2·0 (1)	16 (8)
$O(10)-H(O10)\cdots O(8^{i})$	1·1 (1)	2·82 (1)	1·8 (1)	9 (8)
$O(11)-H(O11)\cdots O(10^{i})$	1·0 (2)	2·76 (2)	2·4 (2)	61 (10)
$O(12)\cdots O(4^{i})$	—	2·84 (1)	—	—

Symmetry code for *B*: (i) x, y, z; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$.

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Structure of Bis(*O,O'*-diisopropyl phosphorodithioato)nickel(II), $Ni[S_2P(O^iC_3H_7)_2]_2$

By Bernard F. Hoskins and Edward R. T. Tiekink

Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, *Australia*

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Abstract. $M_r = 485{\cdot}29$, monoclinic, $C2/c$, $a = 14{\cdot}047\,(2)$, $b = 10{\cdot}338\,(3)$, $c = 16{\cdot}807\,(3)$ Å, $\beta = 109{\cdot}71\,(1)°$, $U = 2298\,(2)$ Å^3, $D_m = 1{\cdot}36\,(2)$, $Z = 4$, $D_x = 1{\cdot}402\,(1)$ Mg m^{-3}, Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 5{\cdot}86$ mm^{-1}, $T = 295\,(2)$ K, $F(000) = 1016$, $R = 0{\cdot}065$ for 1751 observed reflections with $I \geq 3\sigma(I)$. Crystals contain discrete molecules of the title compound with the two dithiophosphate ligands chelating the Ni atom in the expected square-planar array with equivalent Ni—S distances of average value 2·221 (1) Å.

Introduction. Nickel(II) dithiophosphates and dithiophosphinates of the general formula Ni(RR'dtp)$_2$ have been the subject of extensive crystallographic studies. Amongst the complexes which have been structurally characterized are the following: (i) $R=R'$: CH_3 (Jones, Ansell & Katz, 1969), CH_2CH_3 (Shetty & Fernando, 1969), C_6H_5 (Porta, Sgamellotti & Vinciguerra, 1968), OCH_3 (Kastalsky & McConnell, 1969), OCH_2CH_3 (Fernando & Green, 1967; McConnell & Kastalsky, 1967); and (ii) $R{\neq}R'$: CH_3, C_4H_3S (Wunderlich & Wussow, 1979), CH_3, CH_2CH_3 (Wunderlich, 1980), and CH_3, $N(CH_3)_2$ (Seel & Zindler, 1980). In all of the above structures the 1,1-dithiolate ligand chelates the Ni atom with equivalent Ni—S bonds. Recently the structure of the Ni^{II} complex where $R{=}CH_2CH_3$, $R'{=}O^iC_3H_7$ (1) has been reported (Bone, Sowerby, Constantinescu & Haiduc, 1979) in which marked asymmetry is apparent in the mode of coordination of the dithiophosphate ligand: Ni—S 2·262 (1) and 2·116 (1) Å. When $R{=}R'{=}CH_2CH_3$ (Shetty & Fernando, 1969) no special features are observed in the structure to account for this anomalous chelation and it was therefore of interest to ascertain whether the unusual coordination mode noted for (1) is due to the influence of the relatively bulky isopropyl substituents. We therefore have undertaken a crystal structure determination of the Ni^{II} complex where $R{=}R'{=}O^iC_3H_7$, hereafter Ni$\{(C_3H_7O)_2dtp\}_2$.

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Experimental. Ni$\{(C_3H_7O)_2$dtp$\}_2$ was prepared according to the literature method (Francis, Tincher, Wagner, Wasson & Woltermann, 1971), m.p. 414 (2) K. Suitable crystals for X-ray analysis were grown from the slow evaporation of a chloroform solution of the compound. Density measured in aqueous zinc bromide solution. Crystal 0·13 × 0·16 × 0·20 mm. Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/A computer, Cu $K\alpha$ radiation (ω:2θ scan, $2 \leq \theta \leq 70°$). Cell parameters determined by a least-squares procedure on 25 reflections (Cu $K\alpha$, $11 \leq \theta \leq 35°$). The $I \geq 3\sigma(I)$ criterion applied to 2190 unique reflections, $R_{\rm amal} = 0{\cdot}051$, which were derived from the 2906 reflections measured in the ranges of indices $-1 \leq h \leq 17, -1 \leq k \leq 12, -20 \leq l \leq 20$, resulting in 1751 reflections. No significant variation in the intensities of any of the standard reflections ($31\bar{5}$, $31\bar{6}$, $11\bar{4}$) occurred during the data collection; intensity data corrected for Lorentz and polarization effects and for absorption (max. and min. transmission factors 0·5813 and 0·3088). Structure solved by normal Fourier methods and refined using the full-matrix least-squares procedure based on F. Anisotropic thermal parameters for all non-hydrogen atoms and H atoms included at their calculated positions. At convergence $R = 0{\cdot}065$, $wR = 0{\cdot}065$ $\{w = 2{\cdot}1/[\sigma^2(F) + 0{\cdot}001|F|^2]\}$, and $S = 2{\cdot}93$. Attempts to refine the structure in space group Cc were unsuccessful since convergence was not achieved due to gross correlation; this result strongly supports the initial choice of space group as $C2/c$. Analysis of variance showed no special features. Max. residual electron density in final difference map 0·67 e Å^{-3} (min. −0·75 e Å^{-3}) and $(\Delta/\sigma) \leq 0{\cdot}001$. Scattering factors for H, C, O, S and P given in *SHELX76* (Sheldrick, 1976), that for neutral Ni corrected for anomalous dispersion (Hamilton & Ibers, 1974). University of Melbourne's CYBER 730–175 computer system with *SHELX76* (Sheldrick, 1976).

Discussion. Fractional atomic coordinates are given in Table 1* and the numbering scheme is shown in Fig. 1. Interatomic distances and bond angles are given in Table 2.

Crystals of Ni$\{(C_3H_2O)_2$dtp$\}_2$ consist of discrete molecules of the compound separated at distances commensurate with those expected from van der Waals radii. The Ni atom is located at the centre of symmetry at ($\frac{1}{4}$, $\frac{1}{4}$, 0) and as a consequence the four S donor atoms coordinate in a perfect planar array; however, there is distortion from the ideal square geometry which arises from the minor steric constraints imposed by the restricted bite distance of the dithio chelate S···S bite distance 3·088 (2) Å. The dithiophosphate ligand chelates the Ni atom with equivalent Ni—S distances similar to those found for analogous Ni$^{\rm II}$ complexes. It is noteworthy that the associated S—P bonds are also equivalent and these observations together with the overall planarity of the Ni(S$_2$P)$_2$ moiety suggest substantial delocalization of π electrons throughout the two NiS$_2$P four-membered rings.

Table 1. *Fractional atomic coordinates and B_{eq} (Å^2) values*

$B_{\rm eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$

	x	y	z	$B_{\rm eq}$
Ni	0·25	0·25	0·0	3·38
S(1)	0·3587 (1)	0·2032 (1)	0·1276 (1)	4·54
S(2)	0·1961 (1)	0·0474 (1)	−0·0089 (1)	4·53
P(1)	0·2948 (1)	0·0288 (1)	0·1077 (1)	3·97
O(1)	0·2474 (2)	−0·0164 (3)	0·1749 (2)	5·20
C(1)	0·1630 (4)	0·0544 (6)	0·1875 (3)	5·80
C(2)	0·1991 (6)	0·1039 (9)	0·2770 (4)	8·51
C(3)	0·0751 (5)	−0·0393 (9)	0·1672 (5)	8·73
O(2)	0·3710 (2)	−0·0862 (3)	0·1197 (2)	5·03
C(4)	0·4431 (4)	−0·0913 (5)	0·0736 (3)	5·34
C(5)	0·4225 (6)	−0·2110 (7)	0·0211 (5)	8·35
C(6)	0·5466 (5)	−0·0835 (9)	0·1375 (4)	8·30

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Ni—S(1)	2·227 (1)	Ni—S(2)	2·216 (1)
S(1)—P(1)	1·991 (2)	S(2)—P(1)	1·993 (1)
P(1)—O(1)	1·564 (3)	P(1)—O(2)	1·566 (3)
O(1)—C(1)	1·467 (6)	O(2)—C(4)	1·470 (5)
C(1)—C(2)	1·506 (8)	C(4)—C(5)	1·490 (8)
C(1)—C(3)	1·515 (9)	C(4)—C(6)	1·490 (8)
S(1)—Ni—S(2)	88·10 (4)	O(1)—P(1)—O(2)	96·9 (2)
S(1)—Ni—S(2′)	91·90 (4)	P(1)—O(1)—C(1)	121·2 (3)
Ni—S(1)—P(1)	84·94 (4)	O(1)—C(1)—C(2)	107·3 (4)
Ni—S(2)—P(1)	85·21 (4)	O(1)—C(1)—C(3)	106·6 (5)
S(1)—P(1)—S(2)	101·7 (1)	C(2)—C(1)—C(3)	114·6 (5)
S(1)—P(1)—O(1)	115·3 (1)	P(1)—O(2)—C(4)	121·5 (3)
S(1)—P(1)—O(2)	114·6 (1)	O(2)—C(4)—C(5)	108·1 (4)
S(2)—P(1)—O(1)	114·5 (1)	O(2)—C(4)—C(6)	107·4 (4)
S(2)—P(1)—O(2)	114·7 (1)	C(5)—C(4)—C(6)	114·8 (6)

S(2′) is related by centre of symmetry.

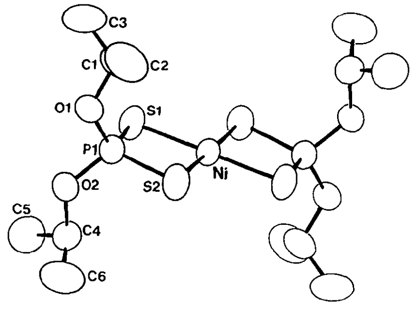

Fig. 1. The numbering scheme used for Ni$\{(C_3H_7O)_2$dtp$\}_2$; note that the Ni atom is located at a site of symmetry $\bar{1}$ (Johnson, 1971).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and mean-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39833 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Although the S_2P moiety is planar, the geometry about the P atom is distorted tetrahedral and as such would be expected to be sp^3 hybridized; therefore, the electronic nature of the individual substituents on the P atom, R and R', would not be expected to effect one Ni—S bond in isolation, as has already been noted for at least three compounds listed in the *Introduction*. As a consequence, it would seem unlikely that the asymmetry found for (1) is electronic in nature.

Clearly there are no outstanding features in the structure of $Ni({}^{i}Prdtp)_2$ that may account for the unusual coordination found for (1) since the presence of the two large isopropyl groups does not impose any obvious steric constraints and hence there is no apparent reason for the asymmetry observed for (1).

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Pentakis(imidazole)copper(II) Monophenyl Phosphate Tetrahydrate, $[Cu(C_3H_4N_2)_5][P(C_6H_5O)O_3].4H_2O$

BY TADEUSZ GŁOWIAK* AND IRENA WNĘK

Institute of Chemistry, F. Joliot-Curie 14, *University of Wrocław*, 50-383 *Wrocław, Poland*

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Abstract. $M_r = 648{\cdot}2$, monoclinic, $P2_1/c$, $a = 14{\cdot}134\,(5)$, $b = 9{\cdot}229\,(3)$, $c = 24{\cdot}150\,(8)$ Å, $\beta = 110{\cdot}60\,(5)°$, $V = 2948{\cdot}8\,(9)$ Å^3, $Z = 4$, $D_m = 1{\cdot}46\,(1)$, $D_x = 1{\cdot}460$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}89$ mm^{-1}, $F(000) = 1348$, $T = 301$ K, $R = 0{\cdot}050$ for 3830 unique observed reflections. The Cu atom is coordinated to the five planar imidazole ligands in rather strongly distorted (4 + 1) symmetry, Cu—N distances 2·028 (4), 2·036 (4), 2·036 (5), 2·062 (4) and 2·230 (5) Å, respectively. The crystal structure is strongly stabilized by a three-dimensional network of hydrogen bonds of the N—H···O(phosphate), O—H···O(water) and O—H···O(phosphate) types.

Introduction. The imidazole group of the histidine side chain is one of the most important binding sites for copper(II) in many metalloproteins and metal–protein complexes.† The effectiveness of the imidazole group in acting as a metal-binding site has been attributed to its great flexibility, its availability at physiological pH (p*K ca* 7·0), and its capacity to form both σ and π bonds with metal ions (Eichhorn, 1973).

Although the detailed structures of a number of bis-, tris-, tetrakis-, hexakis- and some polynuclear-(imidazole)–copper(II) complexes are known (McFadden, McPhail, Garner & Mabbs, 1976; Fransson & Lundberg, 1978; and references cited therein), no structural information has been presented for a pentakis(imidazole)copper(II) cation.

We now report the structure of this cation following an X-ray crystallographic study of the title compound to provide additional precise values for copper(II)–imidazole bond lengths.

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* To whom correspondence should be addressed.

† A list of examples of such binding with appropriate references has been deposited (Table 3). See deposition footnote.

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