The Crystal and Molecular Structure of
Bis-(o,o'-diethyl-dithiophosphato)-1,10-phenanthrolinenickel(II)

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The crystal structure of the compound $C_{20}H_{28}N_2NiO_4P_2S_4$ has been determined by X-ray diffraction methods. The complex crystallizes in the space group $C2/c$ with four molecules in a unit cell of dimensions $a=15\cdot500$ (8), $b=17\cdot400$ (9), $c=10\cdot347$ (5) Å, $\beta=101\cdot210$ (5)°. The structure was solved initially from the three-dimensional Patterson function, computed from 2605 data collected on a single diffractometer and corrected for absorption. Refinement proceeded by successive cycles of structure factors and difference Fourier synthesis followed by full-matrix least-squares procedures. The unit cell contains the *d* and *l* isomers each of which are in the *cis* configuration. The nickel atom lies on a twofold axis of symmetry, which passes through the 1,10-phenanthroline molecule. The effect of increased coordination on the Ni–S bond distance is shown. The final *R* is 0·059.

Introduction

Recently the crystal structure analysis of the low spin square-planar bis-(o,o'-diethyldithiophosphato)nickel-(II) and bis-(o,o'-dimethyldithiophosphato)nickel(II) (McConnell & Kastalsky, 1967; Fernando & Green, 1967; Kastalsky & McConnell, 1969) have shown that the Ni–S distances are in the range $2\cdot21-2\cdot24$ Å. As part of an overall program to study the effect of increased coordination number on the detailed geometry of coordination compounds we were led to investigate the structure of the high spin bis-(o,o'-diethyldithiophosphato)-1,10-phenanthrolinenickel(II). There was also some doubt as to whether an octahedral or binuclear complex had been isolated during the reaction between bis-(o,o'-diethyldithiophosphato)nickel(II) and 1,10-phenanthroline.

The compound, which was supplied by Professor Livingstone and Miss A. Mihkelson of this University was prepared by dissolving $Ni(dtp)_2$ (0·001 mole) in the minimum quantity of hot 95% ethanol and adding an ethanolic solution of 1,10-phenanthroline (0·001 mole). The green crystalline compound was filtered, washed with ethanol and dried in vacuo over phosphorus pentoxide. This compound was first isolated by Jørgensen (1963) as bright green crystals. The crystals were ground in a spherizer and a suitable sphere ($\mu R=0\cdot53$) was selected

Experimental

Crystal data

Bis-(o,o'-diethyldithiophosphato)-1,10-phenanthrol-ine-nickel(II)

$Ni[(C_2H_5O)_2PS_2]_2C_{12}H_8N_2$, F.W. 609·33

Unit-cell dimensions at 20 °C

$a=15\cdot500(8)$ Å
$b=17\cdot400(9)$
$c=10\cdot347(5)$
$\beta=101\cdot210(5)°$

$\varrho(\text{obs}) = 1\cdot3$ g.cm^{-3}
$\varrho(\text{calc}) = 1\cdot26$ g.cm^{-3}
$\mu R = 0\cdot53$
$Z = 4$

Space group from systematic absences is $C2/c$ or Cc.

The unit-cell dimensions and final intensity data were measured on a four-circle Siemens automatic single-crystal diffractometer using Cu $K\alpha$ radiation.

The unit-cell constants were calculated from the observed θ values of selected high angle reflexions. The integrated intensities were recorded by a θ-2θ scan, while the scan range varied from $1\cdot0°$ at low 2θ to $2\cdot8°$ at high 2θ. The scan speed, although automatically controlled by the instrument, was set with an upper time limit of 0·6 sec per step of 0·01°. Any significant drift in crystal orientation requires the calculation of new setting matrices according to the method of Busing & Levy (1967). Absorption, Lorentz and polarization corrections were applied using programs developed in this laboratory. Extinction corrections were not applied to these data.

Determination of the structure

The lower symmetry space group Cc was initially used to locate the Ni atoms from the Patterson synthesis. Successive cycles of structure factors and difference Fourier syntheses located the remaining sulphur and light atoms and it became apparent that each molecule contained a twofold axis of symmetry which passed through each nickel atom. The refinement was therefore carried out in the space group $C2/c$ with the nickel atoms located at special position 4(*e*). The values of $\sum w[|F_{\text{obs}}|-|F_{\text{calc}}|]^2$ were minimized using full-matrix least-squares methods and the final atomic positional parameters and anisotropic thermal parameters are listed in Tables 2 and 3. The residual R has a final value 0·059 for all observed data and these are listed in Table 1.

Table 1. *Observed and calculated structure factors for bis-(o,o'-diethyldithiophosphato)-1,10-phenanthrolinenickel*(II)

The columns from left to right read h,k,l, F_{obs} and F_{calc}, where the values of F_{obs} and F_{calc} are recorded on ten times the absolute scale.

The symbol U denotes an unobserved reflexion and occurs whenever the total peak count recorded for a particular reflexion is less than three standard deviations above the background count.

A total of 2605 data were measured, which included 923 'less than' reflexions.

Table 2. *Fractional atomic coordinates for bis(o-o'-diethyldithiophosphato)1,10-phenanthrolinenickel(II)*

Standard deviations are given in brackets and refer to the last two decimal places in the preceding coordinate.

	x/a	y/b	z/c
Ni	0·0	0·216412 (75)	0·25
S(1)	0·10803 (13)	0·314513 (92)	0·31636 (16)
S(2)	0·90453 (12)	0·225316 (97)	0·41477 (15)
P(1)	0·83528 (13)	0·298082 (96)	0·28986 (17)
N(1)	0·06586 (31)	0·12384 (24)	0·35738 (42)
C(1)	0·33566 (43)	0·44082 (38)	0·46898 (59)
C(2)	0·13031 (40)	0·12774 (35)	0·46614 (52)
C(3)	0·03440 (34)	0·05463 (29)	0·30717 (46)
C(4)	0·63498 (41)	0·48714 (36)	0·48168 (56)
C(5)	0·56625 (40)	0·48470 (32)	0·36252 (55)
C(6)	0·53255 (44)	0·41348 (32)	0·30508 (55)
O(1)	0·73473 (36)	0·27338 (30)	0·24894 (57)
O(2)	0·81643 (34)	0·37755 (25)	0·36094 (45)
C(7)	0·60706 (56)	0·19922 (56)	0·22182 (78)
C(8)	0·69839 (63)	0·20357 (64)	0·2473 (11)
C(9)	0·89308 (69)	0·42567 (49)	0·4170 (10)
C(10)	0·86877 (88)	0·49266 (67)	0·4230 (19)

Table 3. *The tensor components* $(\times 10^3)$ *describing the anisotropic vibration of the atoms in cis-bis(diethyl-dithiophosphato)-1,10-phenanthrolinenickel(II)*

The components U_{ij} are those occurring in the temperature factor $\exp[-2\pi^2(h^2a^2u_{11}+2hka^*b^*U_{12}+\ldots)$ so that for instance U_{11} is the mean square amplitude of vibration parallel to a^*.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{12}	U_{23}
Ni	83	40	46	0	−3	0
S(1)	83	46	50	−9	−3	−5
S(2)	81	59	44	7	1	4
P	67	46	69	3	−5	−5
N	67	41	49	62	−1	3
C(1)	77	70	59	0	−6	0
C(2)	68	73	42	2	−7	17
C(3)	56	42	40	5	0	0
C(4)	76	69	51	0	−2	0
C(5)	72	45	53	0	1	2
C(6)	105	46	64	−4	−1	−2
O(1)	97	71	171	−5	−28	16
O(2)	111	59	100	7	9	−3
C(7)	106	170	112	−22	16	−11

Table 3 *(cont.)*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(8)	87	144	247	−7	−11	16
C(9)	157	67	199	−11	−8	−26
C(10)	201	102	585	−19	36	−67

Atomic scattering factors for the neutral atoms were taken from *International Tables for X-ray Crystallography* (1962) and anomalous dispersion corrections (Dauben & Templeton 1955) were applied to the Ni and S values. Locally developed programs as well as *ORFLS, ORFFE* and *ORTEP* were used in conjunction with an IBM 360/50 computer.

Results and discussion

An octahedral complex is formed when 1,10-phenanthroline reacts with bis-(o,o'-diethyldithiophosphato)-nickel(II). This complex molecule is shown as a stereo pair in Fig. 1 and contains a twofold axis of symmetry, which passes through the nickel atom and the 1,10-phenanthroline molecule. Each nickel atom is bonded to four sulphur and two nitrogen atoms and both *d* and *l* isomers exist in equal numbers in the unit cell.

Bond distances and angles are given in Tables 4 and 5 and are related to Fig. 2. The Ni–S bond distances of 2·509 (2) and 2·471 (2) Å in the octahedral spin-free molecule Ni(dtp)₂-o-phen are significantly longer than those reported for the square planar spin-paired molecule Ni(dtp)₂, namely 2·233 (4) Å (see Table 6). As a result there are small changes in the geometry of the chelate rings; the S–Ni–S angle in Ni(dtp)₂ decreases from 88·5 (1)° to 80·7 (1)° in Ni(dtp)₂-o-phen and the S–P–S angle increases from 103·1 (2)° to 110·2 (1)° in accordance with the simple electrostatic model proposed by Ooi & Fernando (1967) to explain similar observations for bis-(o,o'-diethyldithiophosphato)nickel(II)–bispyridine. The P–S distances within the ligand remain the same for both octahedral and square planar complexes and this is in agreement with similar observations made on other complexes (see Table 6). One would expect this to be true for all ligand intramolecular bond distances. In fact this is generally true for ligand bond an-
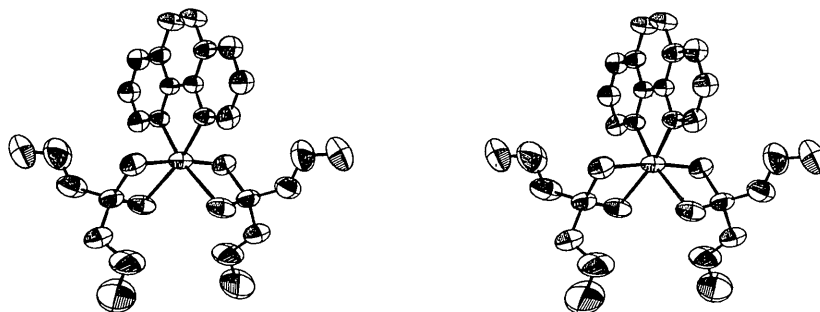

Fig. 1. The bis-(o,o'-diethyldithiophosphato)-1,10-phenanthrolinenickel(II) molecule shown as a stereo pair, which illustrates the configuration. Ellipsoids enclose 50% probability.

gles and corresponding angles associated with the dtp ligand in Ni(dtp)$_2$ and Ni[(dtp)$_2$(o-phen)] are equal. How-

Table 4. *Bond distances ($\mathring{A}$) in a molecule of bis-(o-o'-diethyldithiophosphato)-1,10-phenanthroline nickel(II)*

S(1)—Ni	2·509 (2)	C(1')–C(2')	1·420 (8)
S(2)—Ni	2·471 (2)	C(2')–N(1')	1·354 (6)
N(1) –Ni	2·104 (4)	N(1')–C(3')	1·362 (5)
N(1')–Ni	2·104 (4)	C(3')–C(3)	1·433 (9)
N(1)—C(2)	1·354 (6)	S(1)—P(1)	1·959 (3)
C(2)—C(1)	1·420 (7)	S(2)—P(1)	1·972 (2)
C(1)—C(4)	1·395 (8)	P(1)—O(1)	1·595 (6)
C(4)—C(5)	1·467 (7)	P(1)—O(2)	1·621 (5)
C(5)—C(6)	1·428 (7)	O(1) –C(8)	1·336 (10)
C(6)—C(6')	1·37 (1)	C(8)—C(7)	1·391 (11)
C(6')–C(5')	1·428 (7)	O(2) –C(9)	1·479 (9)
C(5')–C(4')	1·467 (7)	C(9)—C(10)	1·234 (13)
C(4')–C(1')	1·395 (7)		

Superscripts refer to atoms related to those listed in Table 2 by the twofold axis.

ever, the bond distances within the diethoxy moieties of the latter complex are considerably shorter than those of the former. A similar effect was observed by Ito, Igarashi & Hagihara (1969) for the diethoxy moiety in bis-(o,o'- diethyldithiophosphato)zinc(II) and they suggested positional disorder of one of the carbon atoms.

The possibility that the omission of hydrogen atoms from the F_c calculation is responsible for the short C–C distance was tested by refining the data with sin θ/λ values greater than 0·3. The R decreased from 0·066 to 0·055; however the C(9)–C(10) and C(8)–C(7) remained at 1·23 and 1·39. $\mathring{A}$

The thermal parameters of the diethyldithiophosphato groups are generally greater than those of the 1,10-phenanthroline ligand. In particular, the thermal ellipsoid parameters (Table 7) and the probability ellipsoids (50%) shown in Fig. 2 indicate marked anisotropic thermal movements for the terminal ethyl groups. The bond lengths C(7)–C(8) and C(9)–C(10) were there-

Table 5. *Bond angles (°) defined by three atoms in a molecule of bis-(o,o'-diethyldithiophosphato)-1,10-phenanthrolinenickel(II)*

S(1)—Ni——S2	80·7 (1)	C(5')–C(4')–C(1')	117·7 (5)
N(1)—Ni——N(1')	80·1 (3)	C(4')–C(1')–C(2')	121·2 (5)
Ni——N(1)—C(3)	112·0 (3)	C(1')–C(2')–N(1')	119·7 (6)
Ni——N(1)—C(2)	127·1 (4)	C(2')–N(1')–C(3')	120·8 (5)
N(1)—C(2)—C(1)	119·7 (6)	N(1) –Ni——S(1)	93·8 (1)
N(1)—C(3)—C(5)	123·0 (5)	N(1')–Ni——S(1)	167·2 (1)
C(2)—N(1)—C(3)	120·8 (5)	N(1) –Ni——S(2)	96·7 (1)
C(2)—C(1)—C(4)	121·2 (5)	N(1')–Ni——S(2)	88·7 (1)
C(1)—C(4)—C(5)	117·7 (6)	Ni——S(1)—P(1)	84·1 (1)
C(4)—C(5)—C(3)	117·4 (5)	Ni——S(2)—P(1)	84·8 (1)
C(4)—C(5)—C(6)	121·4 (5)	S(1)—P(1)—O(1)	113·3 (3)
C(3)—C(5)—C(6)	121·1 (5)	S(1)—P(1)—O(2)	112·7 (2)
C(5)—C(6)—C(6')	119·8 (3)	S(2)—P(1)—O(1)	112·4 (2)
C(6') –C(6') –C(5')	119·8 (3)	S(2)—P(1)—O(2)	112·0 (2)
C(6') –C(5') –C(3')	121·1 (5)	P(1)—O(1) –C(8)	129·4 (6)
C(6') –C(5') –C(4'')	121·4 (5)	P(1)—O(2) –C(9)	117·2 (5)
		O(1) –C(8)—C(7)	117 (1)
		O(2) –C(9)—C(10)	109 (1)
		S(1)—P(1)—S(2)	110·2 (1)
		O(1) –P(1)—O(2)	95·6 (3)

Superscripts refer to atoms related to those listed in Table 2 by the twofold axis.

Table 6. *Bond distance comparisons between some square planar and octahedral complexes of* Ni(II)

Square-planar	Distance	Compound	Reference
Ni–S	2·233 (4) $\mathring{A}$	Bis-(o,o'-diethyldithiophosphato)Ni(II)	McConnell & Kastalsky (1967)
	2·222 (2)	Bis-(o,o'-dimethyldithiophosphato)Ni(II)	Kastalsky & McConnell (1969)
	2·238 (4)	Bis(diphenyldithiophosphato)Ni(II)	Porta, Sgamellotti & Vinciguerra (1968)
S–P	1·989 (5)	Bis-(o,o'-diethyldithiophosphato)Ni(II)	McConnell & Kastalsky (1967)
	1·981 (2)	Bis-(o,o'-dimethyldithiophosphato)Ni(II)	Kastalsky & McConnell (1969)
Octahedral			
Ni–S	2·490 (2)	Bis-(o,o'-diethyldithiophosphato)1,10-phenanthroline Ni(II)	Present paper
	2·49 (1)	Bis-(o,o'-diethyldithiophosphato)bis-pyridine Ni(II)	Ooi & Fernando (1967)
	2·460 (4)	Dichlorotetrakisthiourea Ni(II)	Lopez, Castro & Truter (1963)
S–P	1·965 (2)	Bis-(o,o'-diethyldithiophosphato)1,10-phenanthroline Ni(II)	Present paper
	1·99 (1)	Bis(diethyldithiophosphato)bis-pyridine Ni(II)	Ooi & Fernando (1967)

fore corrected for riding motion according to the method of Busing & Levy (1964) and the results, given in Table 8, are in accord with the accepted single bond C–C distance of 1·54 Å (Sutton, 1958).

In view of the magnitude of the corrections to these bond lengths due to thermal motion, the standard deviations listed in Table 4 from *ORFFE.* output must be considered as underestimations.

Table 7. *Principal axes of thermal ellipsoids*

The root mean square displacement U_i corresponds to the ith principal axis of the ellipsoid, and O_{ia}, O_{ib}, O_{id} are angles between the ith axis and the crystallographic axes a, b and an axis d normal to a and b. The B_i's are equal to the corresponding $8\pi^2 U_i^2$.

|	i	B_i	U_i	O_{ia}	O_{ib}	O_{id}
Ni	1	3·209 Å²	0·2016	90·0°	63·5°	103·4°
	2	3·260	0·2032	107·0	98·3	61·1
	3	7·549	0·3092	17·0	28·0	32·5
S(1)	1	3·146	0·1996	75·1	61·7	116·8
	2	5·260	0·2581	88·0	110·9	110·3
	3	10·393	0·3628	15·0	36·4	34·7
S(2)	1	3·508	0·2108	104·7	84·9	71·5
	2	5·424	0·2621	76·5	95·4	43·8
	3	7·949	0·3173	20·1	7·4	52·0
P(1)	1	3·439	0·2087	106·2	78·7	99·8
	2	4·405	0·2362	117·3	119·9	69·6
	3	8·427	0·3267	32·4	32·4	22·8
N(1)	1	2·820	0·1890	101·7	76·0	84·7
	2	3·718	0·2170	112·5	121·8	67·7
	3	6·186	0·2799	25·7	35·5	23·0
C(1)	1	3·663	0·2154	61·6	74·6	105·9
	2	5·574	0·2657	87·3	112·4	68·2
	3	7·760	0·3135	28·6	27·7	27·5
C(2)	1	2·390	0·1740	62·7	76·9	105·9
	2	5·524	0·2645	78·8	102·3	56·6
	3	7·471	0·3076	29·9	18·1	37·9
C(3)	1	2·984	0·1944	69·0	82·9	111·4
	2	3·231	0·2023	92·1	116·7	70·3
	3	5·134	0·2550	21·1	27·7	29·8
C(4)	1	3·646	0·2149	67·6	77·9	113·1
	2	5·428	0·2622	92·1	118·4	76·9
	3	7·111	0·3001	22·5	31·3	27·0
C(5)	1	3·289	0·2041	106·9	80·3	92·3
	2	4·371	0·2353	101·8	109·3	55·5
	3	6·359	0·2838	20·8	21·8	34·5
C(6)	1	3·432	0·2085	79·6	56·7	107·1
	2	4·801	0·2466	102·5	86·7	63·9
	3	9·534	0·3475	16·4	33·5	31·9
O(1)	1	4·169	0·2298	51·9	75·4	84·8
	2	5·370	0·2608	120·3	143·5	90·8
	3	20·096	0·5045	52·8	57·3	5·3
O(2)	1	4·283	0·2329	105·3	79·5	118·3
	2	7·929	0·3169	105·2	95·8	60·0
	3	9·502	0·3469	21·8	12·0	43·6
C(7)	1	6·631	0·2898	26·1	6·0	59·5
	2	8·191	0·3221	83·5	84·5	35·3
	3	15·495	0·4430	115·1	87·6	106·1
C(8)	1	5·919	0·2738	22·9	35·1	71·1
	2	10·606	0·3665	90·3	117·9	88·8
	3	23·177	0·5418	112·9	109·5	161·1
C(9)	1	3·273	0·2036	76·3	55·6	108·5
	2	11·807	0·3867	140·8	116·6	105·6
	3	19·818	0·5010	125·8	133·9	155·4
C(10)	1	5·050	0·2529	80·4	51·1	106·9
	2	16·103	0·4516	169·0	141·4	131·4
	3	49·527	0·7920	95·4	107·9	133·7
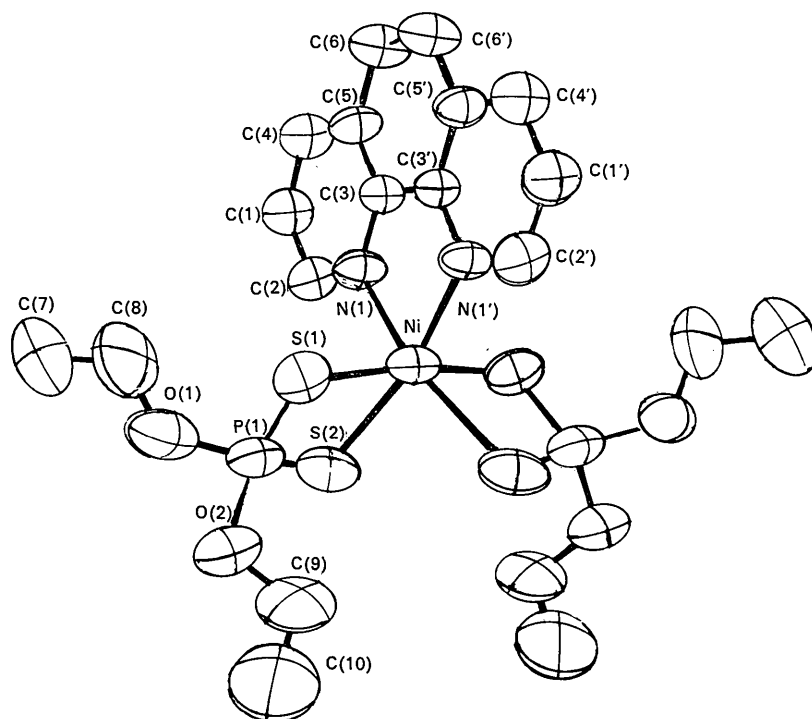
Fig. 2. A single view of the bis-(o,o'-diethyldithiophosphato)-1,10-phenanthrolinenickel(II) molecule. The bond distances Å and angles (°) in Tables 4 and 5 are related to Fig. 2.

Table 8. Bond lengths corrected for riding motion

Bond length	Uncorrected	Lower bound	Riding motion	Upper bound
C(7)–C(8)	1·39 Å	1·49 Å	1·54 Å	1·64 Å
C(9)–C(10)	1·23	1·40	1·57	1·74

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