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Structure of Bis(μ-η³-allyl)-μ₄-sulfido-tetrakis(triphenylphosphine)-tetrapalladium(2 *Pd–Pd*) Tetrahydrofuran Solvate

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Abstract. $[Pd_4S(C_3H_5)_2\{P(C_6H_5)_3\}_4].C_4H_8O$, $M_r = 1659\cdot7$, triclinic, $P\bar{1}$, $a = 15\cdot145$ (2), $b = 20\cdot966$ (4), $c = 14\cdot117$ (2) Å, $\alpha = 100\cdot68$ (1), $\beta = 116\cdot38$ (1), $\gamma = 69\cdot94$ (1)°, $V = 3769\cdot2$ Å³, $Z = 2$, $D_x = 1\cdot46$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 10\cdot76$ cm^{-1}, $F(000) = 1676$, $T = 291$ K. Final $R = 0\cdot058$ ($wR = 0\cdot077$) for 4733 unique observed reflections. The title compound contains a sulfido group bridging two μ-allyl-bis(triphenylphosphine)dipalladium groups. Each Pd atom is coplanar with its four neighbouring atoms, all deviations from the planes being less than $0\cdot1$ Å. One of the bridging allyl groups shows statistical disorder.

Introduction. In the course of an investigation of sulfur-containing polynuclear metal compounds of nickel, palladium and platinum, the characterization of complexes of the type $[(\eta^3\text{-}C_3H_5)MSM'(\eta^3\text{-}C_3H_5)]_x$, where x is unknown, proved to be difficult because of their generally low solubility (Benn, Bogdanović, Göttsch & Rubach, 1983). In order to obtain more structural information we synthesized a phosphine adduct of the palladium complex with the composition, but as yet still unknown structure, $[(\eta^3\text{-}C_3H_5)_2Pd_2S]_x$, by reacting it with an equimolar amount of triphenylphosphine. We were able to isolate crystals of the title compound, the structure of which indicates that a degradation and subsequent rearrangement of the starting material had occurred.

Experimental. The title compound (1) was prepared in a two-step reaction from bis(allyl)palladium (Rubach, 1981). (i) Preparation of $[(\eta^3\text{-}C_3H_5)_2Pd_2S]_x$

(2) (Bogdanović, Goddard, Göttsch, Krüger, Schlichte & Tsay, 1983): a toluene solution of bis-(allyl)palladium was added to a toluene solution of sulfur. A red–violet precipitate of (2) was formed after 12 h. The compound was isolated, washed and dried. (ii) Preparation of (1): triphenylphosphine was added to a suspension of (2) in tetrahydrofuran and allowed to react at room temperature. Yellow crystals of the title compound formed on the side of the glass reaction vessel after several days. The crystal chosen for data collection was $0\cdot15 \times 0\cdot16 \times 0\cdot26$ mm. The unit-cell parameters were obtained by a least-squares fit to the θ values of 74 automatically centred reflections $(3\cdot44 < \theta < 18\cdot4°)$. Intensity data were measured within the range $1\cdot04 < \theta < 21\cdot44°$ on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ X-radiation by a θ–2θ-scan technique in 48 steps, where the time spent measuring the background was half that taken to measure the peak. The intensity of a reflection and its e.s.d. were calculated from $I = \text{INT} - 2(\text{BGL} + \text{BGR})$ and $\sigma(I) = [\text{INT} + 4(\text{BGL} + \text{BGR})]^{0\cdot5}$, where INT, BGL and BGR are the peak intensity, left and right background counts, respectively. The horizontal detector aperture and the ω-scan range varied as $(3\cdot2 + 1\cdot25 \tan\theta)$ mm and $(0\cdot8 + 0\cdot35 \tan\theta)°$. The intensities of three standard reflections, remeasured every 100 reflections, showed no significant variation during data collection. Data were corrected for Lorentz and polarization effects, but not for absorption. $\sigma(F)$ was calculated from $\sigma(F) = [\sigma(I)^2 + (Ik)^2]^{0\cdot5}/2F$, where $k = 0\cdot02$. Of a total of 9038 (h $-15 \rightarrow 13$, k $-21 \rightarrow 21$, l $0 \rightarrow 14$) measured intensities, 4733 satisfied the criterion $I > 2\cdot0\sigma(I)$, and only these were

used in the solution and refinement of the structure. Computer programs used in this investigation include local versions of *DATAP* data-reduction program (Coppens, Leiserowitz & Rabinovich, 1965), *TRACER* (Jacobson & Lawton, 1965) for cell reduction, *SHELX76* (Sheldrick, 1976) for crystal-structure solution and refinement, a modified version of *ORFLS* program for least-squares refinement (Busing, Martin & Levy, 1962), *DAESD* program for distances and angles (Davis & Harris, 1970), *XANADU* molecular-geometry program (Roberts & Sheldrick, 1976), and *ORTEP* thermal-ellipsoid plotting program (Johnson, 1976).

The structure was solved by the heavy-atom method. A difference Fourier synthesis calculated with all the non-H atoms revealed the presence of a solvent molecule in the crystal. Disorder prevented an unequivocal characterization of the molecule, though a five-membered ring could be clearly identified. The crystals were grown from tetrahydrofuran, so a disordered tetrahydrofuran molecule is the most likely candidate. Inclusion of five C atoms (C10–C14) with isotropic thermal parameters in the refinement gave a significant improvement in the weighted R value. Successive substitution of each C atom by an O atom resulted in a poorer fit, and in each case the temperature factor of the O atom became unrealistically large. Refinement was by blocked least-squares methods, where the function minimized was $\Sigma w(\Delta F)^2$ with $w = 1/\sigma(F)^2$ and $\Delta F = |F_o| - |F_c|$. The positions of the H atoms were calculated $[d(\text{C—H}) = 0.95 \text{ Å}]$ and included in the refinement with fixed isotropic thermal parameters $[U(\text{H}) = 0.08 \text{ Å}^2]$. Refinement converged at $R = 0.058$ $(wR = 0.077)$ for 418 variables (n) and 4733 reflections (m), and the value of the 'error of fit' $\{S = [\Sigma w(\Delta F)^2/(m - n)]^{0.5}\}$ was 1·24, indicating a slight underestimation of the error of an observation of unit weight. In the final refinement cycle the maximum shift to e.s.d. ratio was 0·05 (0·4 for solvent). A correction for the effects of anomalous dispersion for Pd $(f' -1·177, f'' 1·007)$ and P $(f' 0·09, f'' 0·095)$ was included in the structure-factor calculations. Atomic scattering curves were taken from *International Tables for X-ray Crystallography* (1974). In the final difference Fourier synthesis, peaks of $\pm 1·29 \text{ e Å}^{-3}$ were observed in the vicinity of the Pd atoms. Tables 1 and 2 give the final atomic coordinates and selected interatomic distances and angles.* Fig. 1 shows the molecular structure of (1), and Fig. 2 the packing of molecules in the unit cell.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52015 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters (for* C *and* H *these are the isotropic thermal parameters) with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Pd1	0·5177 (1)	0·1913 (1)	0·4304 (1)	0·054
Pd2	0·4080 (1)	0·1851 (1)	0·5273 (1)	0·055
Pd3	0·2144 (1)	0·3464 (1)	0·3339 (1)	0·051
Pd4	0·3326 (1)	0·3894 (1)	0·5199 (1)	0·050
P1	0·5982 (4)	0·2151 (3)	0·3458 (4)	0·059
P2	0·2957 (4)	0·1818 (2)	0·5890 (4)	0·055
P3	0·1232 (4)	0·2899 (3)	0·1909 (4)	0·062
P4	0·4340 (4)	0·4099 (3)	0·6904 (4)	0·057
S1	0·3785 (3)	0·2809 (2)	0·4420 (4)	0·051
C1	0·609 (2)	0·091 (1)	0·473 (2)	0·071
C3	0·506 (2)	0·087 (1)	0·578 (2)	0·066
C6	0·213 (2)	0·483 (1)	0·499 (2)	0·063
C4	0·106 (2)	0·441 (1)	0·319 (2)	0·065
C110	0·513 (1)	0·2658 (9)	0·226 (1)	0·045
C111	0·538 (2)	0·313 (1)	0·195 (2)	0·062
C112	0·476 (2)	0·346 (1)	0·103 (2)	0·075
C113	0·389 (2)	0·329 (1)	0·040 (2)	0·090
C114	0·360 (2)	0·284 (1)	0·064 (2)	0·089
C115	0·425 (2)	0·250 (1)	0·162 (2)	0·076
C120	0·681 (1)	0·268 (1)	0·432 (1)	0·055
C121	0·773 (2)	0·265 (1)	0·428 (2)	0·062
C122	0·833 (2)	0·305 (1)	0·497 (2)	0·081
C123	0·803 (2)	0·349 (1)	0·569 (2)	0·069
C124	0·710 (2)	0·356 (1)	0·571 (2)	0·074
C125	0·651 (2)	0·312 (1)	0·505 (2)	0·068
C130	0·683 (1)	0·1468 (9)	0·297 (1)	0·045
C131	0·668 (2)	0·136 (1)	0·195 (2)	0·077
C132	0·733 (2)	0·079 (1)	0·162 (2)	0·079
C133	0·813 (2)	0·035 (1)	0·230 (2)	0·078
C134	0·826 (2)	0·043 (1)	0·331 (2)	0·069
C135	0·764 (2)	0·099 (1)	0·368 (2)	0·064
C210	0·359 (1)	0·1388 (9)	0·714 (1)	0·049
C211	0·430 (2)	0·166 (1)	0·796 (2)	0·084
C212	0·477 (2)	0·139 (1)	0·894 (2)	0·095
C213	0·466 (2)	0·083 (1)	0·911 (2)	0·099
C214	0·398 (2)	0·054 (1)	0·830 (2)	0·086
C215	0·340 (2)	0·084 (1)	0·732 (2)	0·063
C220	0·207 (1)	0·2590 (9)	0·616 (1)	0·042
C221	0·185 (1)	0·272 (1)	0·705 (1)	0·054
C222	0·106 (2)	0·329 (1)	0·714 (2)	0·072
C223	0·056 (2)	0·374 (1)	0·641 (2)	0·065
C224	0·075 (2)	0·366 (1)	0·552 (2)	0·078
C225	0·151 (2)	0·309 (1)	0·539 (2)	0·061
C230	0·210 (1)	0·132 (1)	0·503 (1)	0·053
C231	0·238 (2)	0·082 (1)	0·434 (2)	0·065
C232	0·175 (2)	0·044 (1)	0·370 (2)	0·076
C233	0·080 (2)	0·056 (1)	0·365 (2)	0·088
C234	0·049 (2)	0·106 (1)	0·427 (2)	0·102
C235	0·112 (2)	0·144 (1)	0·497 (2)	0·076
C310	0·054 (2)	0·338 (1)	0·069 (2)	0·061
C311	0·099 (2)	0·379 (1)	0·051 (2)	0·069
C312	0·051 (2)	0·416 (1)	−0·039 (2)	0·085
C313	−0·041 (2)	0·409 (1)	−0·110 (2)	0·080
C314	−0·089 (2)	0·371 (1)	−0·099 (2)	0·093
C315	−0·041 (2)	0·335 (1)	−0·008 (2)	0·074
C320	0·196 (2)	0·210 (1)	0·153 (2)	0·062
C321	0·189 (2)	0·190 (1)	0·050 (2)	0·071
C322	0·247 (2)	0·126 (2)	0·024 (2)	0·108
C323	0·315 (2)	0·083 (2)	0·105 (3)	0·114
C324	0·323 (2)	0·098 (1)	0·202 (2)	0·089
C325	0·265 (2)	0·161 (1)	0·228 (2)	0·081
C330	0·023 (2)	0·265 (1)	0·200 (2)	0·058
C331	0·005 (2)	0·205 (1)	0·164 (2)	0·091
C332	−0·079 (3)	0·191 (2)	0·169 (3)	0·117
C333	−0·140 (2)	0·239 (2)	0·211 (2)	0·108
C334	−0·125 (2)	0·299 (2)	0·246 (2)	0·106
C335	−0·039 (2)	0·312 (1)	0·242 (2)	0·086
C410	0·363 (1)	0·4573 (9)	0·770 (1)	0·049
C411	0·282 (2)	0·438 (1)	0·766 (2)	0·071
C412	0·226 (2)	0·470 (1)	0·823 (2)	0·080
C413	0·246 (2)	0·526 (1)	0·883 (2)	0·071
C414	0·321 (2)	0·549 (1)	0·887 (2)	0·094
C415	0·382 (2)	0·514 (1)	0·833 (2)	0·090
C420	0·520 (1)	0·4595 (9)	0·709 (1)	0·052
C421	0·492 (2)	0·506 (1)	0·632 (2)	0·066
C422	0·549 (2)	0·547 (1)	0·643 (2)	0·073
C423	0·636 (2)	0·543 (1)	0·733 (2)	0·063
C424	0·667 (2)	0·500 (1)	0·809 (2)	0·078
C425	0·610 (2)	0·460 (1)	0·800 (2)	0·063
C430	0·524 (1)	0·3373 (9)	0·772 (1)	0·048

Table 1 (cont.)

	x	y	z	U_{eq}(Å²)
C431	0·574 (2)	0·284 (1)	0·725 (2)	0·072
C432	0·651 (1)	0·227 (1)	0·785 (2)	0·086
C433	0·673 (2)	0·225 (1)	0·890 (2)	0·089
C434	0·622 (2)	0·279 (1)	0·935 (2)	0·085
C435	0·544 (2)	0·333 (1)	0·874 (2)	0·078
C5	0·180 (2)	0·469 (1)	0·390 (2)	0·061
C2a	0·584 (3)	0·102 (2)	0·558 (3)	0·052
C2b	0·536 (4)	0·083 (3)	0·500 (4)	0·084
C10	0·873 (3)	0·139 (2)	0·700 (4)	0·163
C11	0·948 (4)	0·111 (2)	0·668 (4)	0·171
C12	1·014 (4)	0·145 (3)	0·694 (4)	0·212
C13	0·997 (3)	0·194 (2)	0·770 (4)	0·167
C14	0·901 (4)	0·196 (2)	0·774 (4)	0·175

The coordination sphere around the S atom is similar to that observed for other polynuclear complexes containing an S atom bridging two metal—metal bonded species {[CH₃SFe₂(CO)₆]₂S (Coleman, Wojcicki, Pollick & Dahl, 1967), [C₅H₄N(CO)₆Fe₂-μ_4-SFe₂(CO)₆SC₅H₄N] (Le Borgne & Grandjean, 1975), [Fe₄(CO)₁₂S(CSNMe₂)(CNMe₂)] (Dean & Vanderveer, 1978), [Os₆(CO)₁₃(μ_4-S)₂(η-HC=NPh)₂] (Adams & Foust, 1983)}. The sulfido group acts as a formal six-electron donor, and each Pd atom has 16 electrons in its valence shell. The planes passing through Pd1, S1, Pd2 and Pd3, S1, Pd4 are coplanar
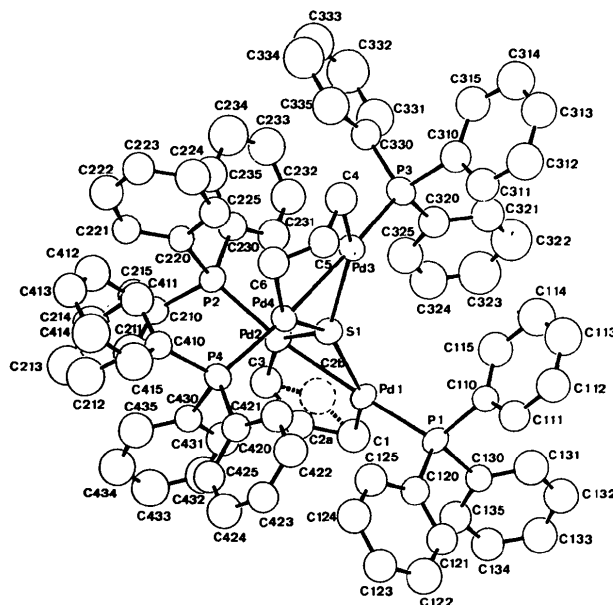
Table 2. Selected interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses

Pd1—Pd2	2·625 (2)	Pd1—P1	2·258 (6)
Pd1—S1	2·342 (5)	Pd1—C1	2·11 (2)
Pd1—C2a	2·48 (4)	Pd1—C2b	2·52 (6)
Pd2—P2	2·252 (6)	Pd2—S1	2·342 (5)
Pd2—C3	2·11 (2)	Pd2—C2a	2·53 (4)
Pd2—C2b	2·45 (6)	Pd3—Pd4	2·639 (2)
Pd3—P3	2·269 (6)	Pd3—S1	2·336 (5)
Pd3—C4	2·07 (2)	Pd3—C5	2·50 (2)
Pd4—P4	2·263 (6)	Pd4—S1	2·353 (5)
Pd4—C6	2·12 (2)	Pd4—C5	2·50 (2)
P1—C110	1·86 (2)	P1—C120	1·85 (2)
P1—C130	1·83 (2)	P2—C210	1·83 (2)
P2—C220	1·82 (2)	P2—C230	1·82 (2)
P3—C310	1·84 (2)	P3—C320	1·80 (2)
P3—C330	1·82 (2)	P4—C410	1·82 (2)
P4—C420	1·84 (2)	P4—C430	1·82 (2)
C1—C2a	1·37 (5)	C1—C2b	1·40 (7)
C3—C2a	1·46 (5)	C3—C2b	1·33 (6)
C6—C5	1·38 (3)	C4—C5	1·35 (3)
C2a—C2b	0·96 (7)	C10—C11	1·31 (8)
C10—C14	1·48 (7)	C11—C12	1·31 (8)
C12—C13	1·40 (8)	C13—C14	1·47 (8)

C1—Pd1—S1	145·1 (7)	C1—Pd1—P1	100·1 (7)
C1—Pd1—Pd2	89·2 (7)	S1—Pd1—P1	114·7 (2)
S1—Pd1—Pd2	55·9 (1)	P1—Pd1—Pd2	170·5 (2)
C3—Pd2—S1	146·0 (7)	C3—Pd2—P2	93·7 (7)
C3—Pd2—Pd1	90·3 (7)	S1—Pd2—P2	120·4 (2)
S1—Pd2—Pd1	55·9 (1)	P2—Pd2—Pd1	172·3 (2)
C4—Pd3—S1	144·2 (7)	C4—Pd3—P3	100·4 (7)
C4—Pd3—Pd4	88·2 (6)	S1—Pd3—P3	115·3 (2)
S1—Pd3—Pd4	56·0 (1)	P3—Pd3—Pd4	168·5 (2)
C6—Pd4—S1	143·6 (6)	C6—Pd4—P4	97·3 (6)
C6—Pd4—Pd3	88·2 (6)	S1—Pd4—P4	118·5 (2)
S1—Pd4—Pd3	55·4 (1)	P4—Pd4—Pd3	169·8 (2)
C130—P1—C120	103·4 (9)	C130—P1—C110	101·0 (9)
C130—P1—Pd1	120·7 (7)	C120—P1—C110	103·3 (9)
C120—P1—Pd1	110·4 (7)	C110—P1—Pd1	115·9 (7)
C230—P2—C220	102·6 (9)	C230—P2—C210	102·6 (9)
C230—P2—Pd2	112·8 (7)	C220—P2—C210	101·9 (9)
C220—P2—Pd2	121·6 (6)	C210—P2—Pd2	113·1 (7)
C330—P3—C320	102 (1)	C330—P3—C310	103 (1)
C330—P3—Pd3	116·5 (7)	C320—P3—C310	104 (1)
C320—P3—Pd3	116·3 (8)	C310—P3—Pd3	113·7 (7)
C430—P4—C420	101·6 (9)	C430—P4—C410	101·7 (9)
C430—P4—Pd4	118·2 (7)	C420—P4—C410	103·8 (9)
C420—P4—Pd4	115·2 (7)	C410—P4—Pd4	114·3 (7)
Pd4—S1—Pd3	68·5 (1)	Pd4—S1—Pd2	119·0 (2)
Pd4—S1—Pd1	144·0 (2)	Pd3—S1—Pd2	123·5 (2)
Pd3—S1—Pd1	140·5 (2)	Pd2—S1—Pd1	68·2 (1)
C4—C5—C6	133 (2)	Pd4—C5—Pd3	63·8 (5)
C3—C2a—C1	134 (4)	Pd2—C2a—Pd1	63 (1)
C3—C2b—C1	145 (5)	Pd2—C2b—Pd1	64 (1)
C14—C10—C11	107 (5)	C12—C11—C10	116 (5)
C13—C12—C11	106 (5)	C14—C13—C12	108 (5)
C13—C14—C10	101 (4)		

Fig. 1. The molecular structure of (1).

Discussion. The results of the X-ray analysis reveal a structure in which a sulfido group is bonded to four Pd atoms. The coordination geometry of the Pd atoms is square planar with a maximum deviation of 0·1 Å from the least-squares plane.
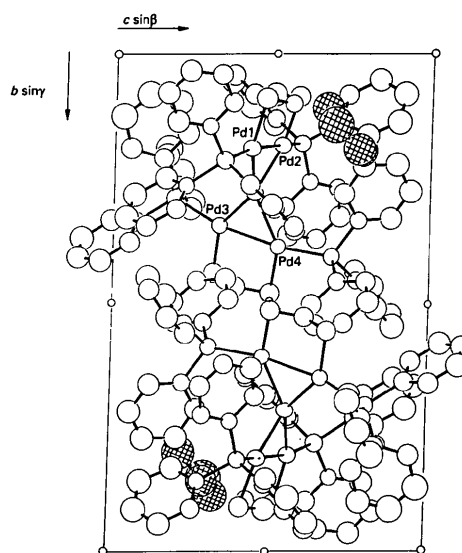

Fig. 2. The packing of (1) in the unit cell, viewed down a looking towards the origin.

with the terminal C atoms of their neighbouring allyl groups (max. deviation 0·05 Å), and make an angle of 82·3° to one another.

Each of the allyl groups bridges two metal atoms. The IR spectra of $[(C_3H_5Pd)_2S]_x$ indicated that all the allyl groups are μ_3-bonded to the Pd atoms (Bogdanović et al., 1983) so it would appear that during the preparation of the compound rearrangement of the allyl groups has occurred.

Statistical disorder of the meso C atom in one allyl group and high standard deviations for the coordinates of the C atoms in the other unfortunately prevent a detailed discussion of geometry of the allyl groups. The Pd—Pd distance at 2·63 (1) Å (mean), however, is similar to that in other compounds containing a Pd—Pd bond bridged by an allyl group {2·686 (7), $[\mu$-$C_3H_5)(\mu$-I)Pd_2[P(C_6H_5)_2]$ (Kobayashi, Iitaka & Yamazaki, 1972); 2·679, $[(C_5H_5)\{2$-(CH_3)-$C_3H_4\}Pd_2\{P(C_6H_5)_3\}_2]$; 2·689, $[(C_5H_5)\{2$-$(CH_3)C_3H_4\}$-$Pd_2P(OC_6H_4$-o-$CH_3)_3]_2$ (Werner, Kühn, Tune, Krüger, Brauer, Sekutowski & Tsay, 1977); 2·720 (1) Å, $[\eta^3$-$C_3H_5PdP(C_6H_5)_3]_2$ (Jolly, Krüger, Schick & Wilke, 1980)}.

Other bond distances and angles in the molecule are as expected. There are no intermolecular contacts between non-H atoms of less than 3·2 Å.

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Aquabis(pyridine-2-carboxamide oxime)copper(II) Chloride

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Abstract. $[Cu(C_6H_7N_3O)_2(H_2O)]Cl_2$, $M_r = 426·75$, monoclinic, $C2/c$, $a = 16·854$ (7), $b = 7·091$ (3), $c = 14·849$ (8) Å, $\beta = 106·39$ (4)°, $V = 1702$ (1) Å³, $Z = 4$, $D_m = 1·66$, $D_x = 1·665$ g cm⁻³, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 16·1$ cm⁻¹, $F(000) = 868·00$, room temperature, $R = 0·041$ for 1570 unique reflections. In forming the complex the oxime group of the ligand is not deprotonated. The coordination about copper(II) is distorted square pyramidal, with the bidentate ligand bound to the metal through the pyridine and oxime N atoms, the water oxygen occupying the axial position. The Cu—N(oxime), Cu—N(py) and Cu—O(w) bond lengths are 1·971 (2), 2·009 (2) and 2·284 (4) Å, respectively. The amide oxime NH_2 group is not used in the complexation.

Introduction. Amide oximes are versatile ligands capable of binding metal ions through the oxime N, oxime O and amide N atoms. Since the amide oxime group may or may not deprotonate upon coordination, formation of a large number of different mononuclear and polynuclear metal complexes is possible (Chakravorty, 1974).

As part of our study of the structural and equilibrium characteristics of copper(II) and