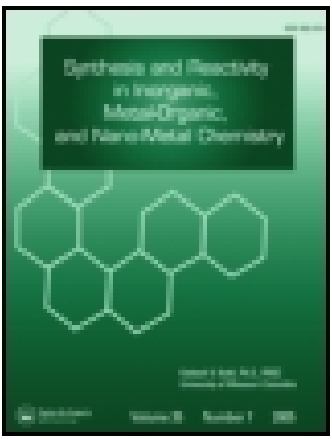

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Synthesis and Characterization of Copper(I) and Silver(I) Complexes Containing Thioamide Ligands

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SYNTHESIS AND CHARACTERIZATION OF COPPER(I) AND SILVER(I) COMPLEXES CONTAINING THIOAMIDE LIGANDS

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ABSTRACT

Mononuclear complexes of the type $(Ph_3P)_2MLX$, where M = Cu, Ag; X = Cl, Br; L = dithiooxamide, thiourea, aminothiourea, have been synthesized and characterized by elemental analyses and IR spectra. The X-ray crystallographic structure determination of $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$ is reported. Dithiooxamide acts as a monodentate ligand through one S atom coordinated to Cu. The coordination of the Cu atom is a distorted tetrahedron with a Cu-Br distance of 2.482(3) and Cu-S distance of 2.356(5) Å.

INTRODUCTION

Recent studies on copper(I) and silver(I) complexes and clusters in our laboratory demonstrated that some substances containing polydentates such as $MO_nS_{4-n}^{2-}$ (M = Mo, W) exhibit strong nonlinear optical properties. Examples are $MS_3OCu_2(PPh_3)_3$ (M = Mo, W) [1] and $Mo_2S_8Ag_4(PPh_3)_4$ [2]. In attempts to imitate the polydentate $MO_nS_{4-n}^{2-}$ (M = Mo, W) with dithiooxamide [3] and/or synthesize thioamide containing Cu(Ag)-Mo(W)-S clusters we obtained thioamide complexes of the type $(Ph_3P)_2MLX$, where M = Cu, Ag; L = thioamide; X = Cl, Br. In this paper we would like to report their synthesis and

characterization as well as the result of the X-ray crystal structure determination of $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$.

RESULTS AND DISCUSSION

Syntheses and Reactions of the Complexes

$(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$ *(1)*, $(Ph_3P)_2Ag(C_2H_4N_2S_2)Cl$ *(2)* and $(Ph_3P)_2Cu(CH_4N_2S)Br$ *(3)* were obtained from the reactions of $(Ph_3P)_2MNO_3$ (M = Cu, Ag) with thioamide and Me_4NX in CH_2Cl_2 solution, which take place as shown below:

$$(Ph_3P)_2MNO_3 + H_2N\text{-}\overset{\overset{S}{\|}}{C}\text{-}R + X^- \xrightarrow{CH_2Cl_2} (Ph_3P)_2\overset{\overset{X}{|}}{M}\text{-}S{=}\overset{\overset{NH_2}{|}}{C}\text{-}R + NO_3^-$$

$$M = Cu, Ag; \quad R = NH_2, \overset{\overset{S}{\|}}{C}\text{-}NH_2; \quad X = Cl, Br$$

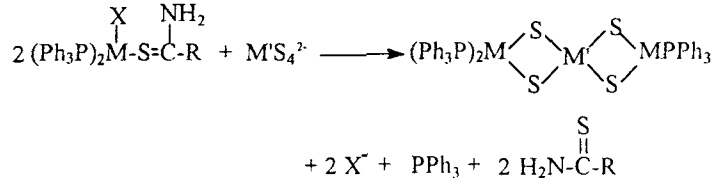
$(Ph_3P)_2Cu(CH_5N_3S)Cl$ *(4)* was prepared by using the new method of "solid state reaction at low temperature", which was developed in recent years and has been applied in synthesizing more than two hundred clusters and coordination compounds[4]. The advantage of using this method is that the reaction can take place without solvent and sometimes generates unusual products[5,6]. Since CuCl is insoluble in dichloromethane and hard to react with other materials, the solid state reaction method was applied to synthesize *(4)*. The reaction is as follows:

$$2\,Ph_3P + CuCl + H_2NHN\overset{\overset{S}{\|}}{C}NH_2 \xrightarrow[\text{Solid State}]{90\,^\circ C,\ 12\ h} \text{Crude Product}$$

$$\xrightarrow[CH_2Cl_2]{\text{Extracted by}} (Ph_3P)_2\overset{\overset{Cl}{|}}{Cu}\text{-}S{=}\overset{\overset{NH_2}{|}}{C}NHNH_2$$

The compositions of all complexes obtained were determined by elemental analyses and IR spectral data listed in Tables I and II, respectively. The complexes are air-stable and soluble in common organic solvents such as acetonitrile, dichloromethane, chloroform and tetrahydrofuran, but insoluble in hexane and ethanol.

Attempting to replace X^- with MoS_4^{2-} or WS_4^{2-} results in $(Ph_3P)_3M_2M'S_4$ (M = Cu, Ag and M' = Mo, W), which are all known compounds[7]. These reactions occur as shown below:



When X^- is substituted, the thioamide ligands are also lost. This indicates that $M'S_4^{2-}$ tends to form bidentate complexes and the coordinating abilities of thioamides are weak compared to those of $M'S_4^{2-}$ and/or PPh_3. Furthermore, it is noteworthy that we have obtained $MoOS_3Cu_2(PPh_3)_2(Py)_2$ from the reaction of $(H_4N)_2MoOS_3$, CuI, PPh_3 and Py[8], but we have never gained analogues with thioamides instead of Py.

Infrared Spectra

The important IR frequencies of these compounds are given in Table II. The characteristic absorption bands of dithiooxamide, thiourea, aminothiourea and Ph_3P are also shown in Table II. The bands of Ph_3P are primarily unchanged before and after coordination, while the bands of thioamide are shifted. The alterations of ν C=S bands appearing at about 1190 cm^{-1} are very significant, whereas the shifts of ν C-N bands are small[9]. This shows that the thioamides coordinate to metal *via* the S atom and not the N atoms, which is consistent with the crystal structure of *(1)* in this work and *(2)*[3].

Molecular Structure of $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$ (1)

The structure of $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$ is shown in Figure 1. It is a mononuclear complex with the Cu atom as coordinating center, which has a tetrahedral coordination involving Br, two P atoms from PPh_3 and one S atom from dithiooxamide. The dithiooxamide acts as a monodentate ligand through one S atom coordinated to Cu and exhibits a *trans* configuration. The S(1)-C(1) distance is slightly longer than that of S(2)-C(2) owing to the influence of the coordination of S(1). The dithiooxamide molecule is almost planar except for a slight deviation of the coordinated S atom from the plane.

The Br-Cu-S, S-Cu-P and Br-Cu-P angles deviate a little (not larger than 6°) from the tetrahedral value, while the P-Cu-P angle is much larger (the deviation is 14.3°) owing to the interactions between the two bulky phosphine ligands. The average Cu-P distance is 2.289(5) Å, which is the usual value found in other Cu(I) compounds containing phosphine ligands, such as $(Ph_3P)_2CuX$[10] and $(Ph_3P)_2CuS_2P(OEt)_2$[11]. Cu-Br and Cu-S distances are 2.482(3) and 2.356(5) Å, respectively, which are comparable to 2.481(5) A for the Cu-Br

Table I. The Analytical Data of Cu(I) and Ag(I) Complexes Containing Thioamide

	Compounds[a]	Empirical formula	Color	M. p. (°C)	Yield (%)	Elemental analyses (%)[b] C	H	N
(1)	$(Ph_3P)_2Cu(dto)Br$	$C_{38}H_{34}CuBrN_2P_2S_2$	red	184	71.8	58.12	4.43	3.60
						(57.90)	(4.35)	(3.55)
(2)	$(Ph_3P)_2Ag(dto)Cl$	$C_{38}H_{34}AgClN_2P_2S_2$	red	213	79.3	58.05	4.39	3.54
						(57.91)	(4.35)	(3.55)
(3)	$(Ph_3P)_2Cu(tu)Br$	$C_{37}H_{34}CuBrN_2P_2S$	color-less	205	84.6	59.97	4.70	4.08
						(59.72)	(4.61)	(3.87)
(4)	$(Ph_3P)_2Cu(atu)Cl$	$C_{37}H_{35}CuClN_3P_2S$	color-less	158	86.5	61.90	4.81	5.78
						(62.18)	(4.94)	(5.88)

[a] dto = $C_2H_4N_2S_2$, dithiooxamide; tu = CH_4N_2S, thiourea; atu = CH_5N_3S, aminothiourea.

[b] Calculated values are given in parentheses.

Table II. Selected IR Data (cm^{-1}) for Thioamide Complexes

Comp.	ν N-H (ν C-H)	δ N-H	ν C-N	ν C=S	ν C=C (Ph)	ν P-C
PPh_3	(3048)				1478, 1411	1095
dto	3300	1585	1430	1190		
(1)	3332, 3132	1577	1432	1180	1478, 1398	1095
(2)	3321 (3059)	1590	1433	1181	1477, 1412	1094
tu	3300	1640, 1590	1430	1090		
(3)	3272, 3179	1609, 1625	1434	1070	1480, 1407	1094
atu	3360, 3250	1645, 1535	1435	1170		
(4)	3268, 3184	1630, 1581	1433	1159	1482	1096
	(3058)	1518				

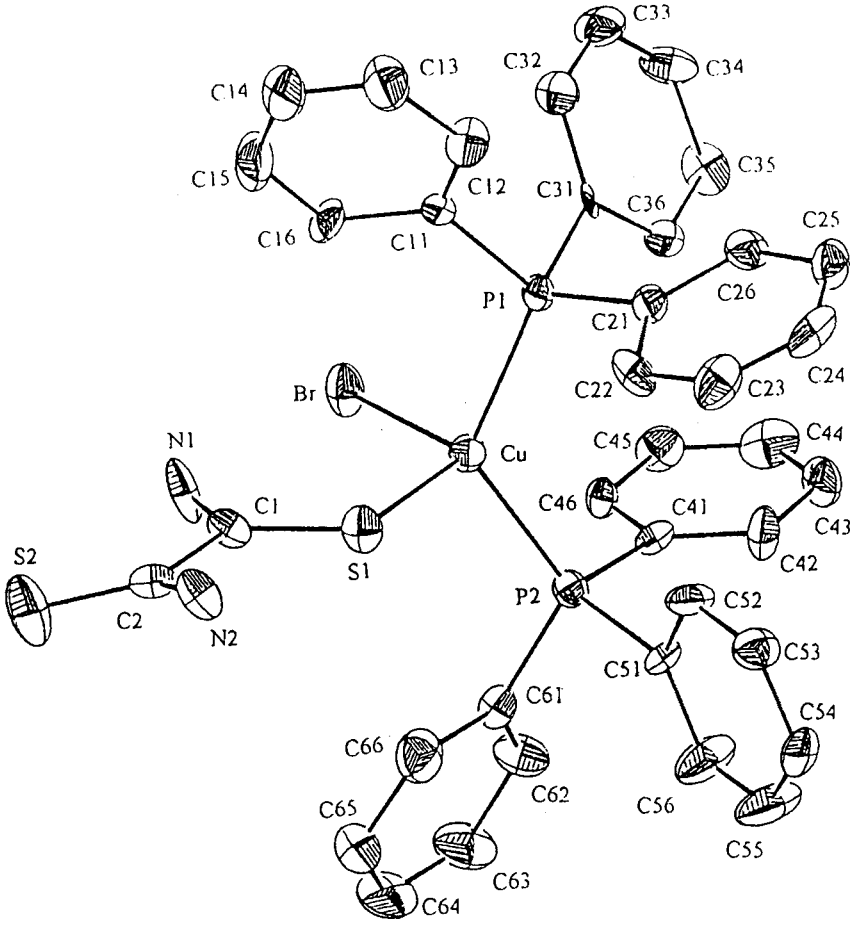


Figure 1. Molecular structure of $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$*(2)*. Displacement ellipsoids are shown at the 30% probability level. H atoms are omitted.

distance found in $(Ph_3P)_3CuBr$[12] and 2.302(4)~2.375(1) Å for the Cu-S distances found in $(Ph_3P)_2Cu(HL)Br$ (HL = 2(1*H*)-pyridinethione, 2(1*H*)-pyrimidinethione, 1,3-dihydro-1-methyl-2*H*-imidazole-2-thione)[13]

There exist intra- and intermolecular hydrogen bond interactions like that in $(Ph_3P)_2Cu(C_2H_4N_2S_2)Cl$[9] between N(1), N(2) and the Br atom in the present structure: N(1)...Br = 3.28(1) Å, Br-H(2)-N1 = 159(1)° and N(2')...Br = 3.34(1) Å, Br-H(3')-N(2) = 158(1)°. From the X-H-N angles and X-N distances, we know that the N-H-Br hydrogen bond is not so strong as that of N-H-Cl. By the linking of N(1)-H-Br, a CuSCN-H-Br ring is formed in the molecule; and by the bridging of N(2)-H-Br, the molecules connect with each other and form an array of polymer chains running along the *a* axis (see Fig. 2).

EXPERIMENTAL

All reagents were of A. R. or C. P. grade and used as received. IR spectra in the 4000-400 cm^{-1} range were obtained on a Nicolet 170sx FT-IR spectrophotometer as KBr pellets. Carbon, hydrogen and nitrogen analyses were performed with a Perkin-Elmer 240c elemental analyser.

Preparation of the Complexes

$(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$ *(1)* and $(Ph_3P)_2Ag(C_2H_4N_2S_2)Cl$ *(2)*. A mixture of $(Ph_3P)_2CuNO_3$ or $(Ph_3P)_2AgNO_3$ (3 mmol), dithiooxamide (0.36 g, 3 mmol) and Me_4NBr or Me_4NCl (3 mmol) in CH_2Cl_2 (50 mL) was stirred for 0.5 h at room temperature and then filtered. $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$ *(1)* and $(Ph_3P)_2Ag(C_2H_4N_2S_2)Cl$ *(2)* crystallized as red crystals while the solution was evaporated slowly in air. The crystals were collected by separating them from the crude products mechanically.

$(Ph_3P)_2Cu(CH_4N_2S)Br$ *(3)*. This compound was prepared in the same way as above with thiourea instead of dithiooxamide, and then crystallized in CH_2Cl_2 as colorless crystals. A selected crystal was scanned on a Enraf-Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation (λ = 0.71073 Å) giving the cell parameters: triclinic, space group $P\bar{1}$, a = 9.71(5), b = 11.97(2), c = 16.08(4) Å, α = 85.3(1), β = 80.7(3), γ = 70.2(2)°, V = 1736(10) $Å^3$. The results of the elemental analyses are listed in Table 1.

$(Ph_3P)_2Cu(CH_5N_3S)Cl$ *(4)*. A well-ground mixture of CuCl (0.10 g, 1 mmol), aminothiourea (0.09 g, 1 mmol) and Ph_3P (0.53 g, 2 mmol) was put into a reaction tube. A white solid was generated by heating the mixture at 90 °C for 12 h under pure nitrogen

Table III. Selected Bond Distances (Å) and Angles (°) for $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$

Br-Cu	2.482(3)	Cu-P(2)	2.280(5)
Cu-P(1)	2.298(5)	Cu-S(1)	2.356(5)
S(1)-C(1)	1.68(2)	S(2)-C(2)	1.63(2)
N(1)-C(1)	1.27(2)	N(2)-C(2)	1.31(2)
C(1)-C(2)	1.56(2)	N(1)-Br	3.28(1)
N(2')-Br	3.34(1)		
P(2)-Cu-P(1)	123.8(2)	P(2)-Cu-S(1)	109.2(2)
P(2)-Cu-Br	104.7(1)	P(1)-Cu-S(1)	104.1(2)
P(1)-Cu-Br	104.0(1)	S(1)-Cu-Br	110.8(1)
C(1)-S(1)-Cu	113.8(5)	N(1)-C(1)-C(2)	116(1)
C(2)-C(1)-S(1)	119(1)	N(1)-C(1)-S(1)	125(1)
N(2)-C(2)-S(2)	128(1)	N(2)-C(2)-C(1)	113(1)
C(1)-C(2)-S(2)	120(1)	N(1)-H(1)-Br	159(1)
N(2')-H(3')-Br	158(1)		

Symmetry code: (i) 1+x, y, z

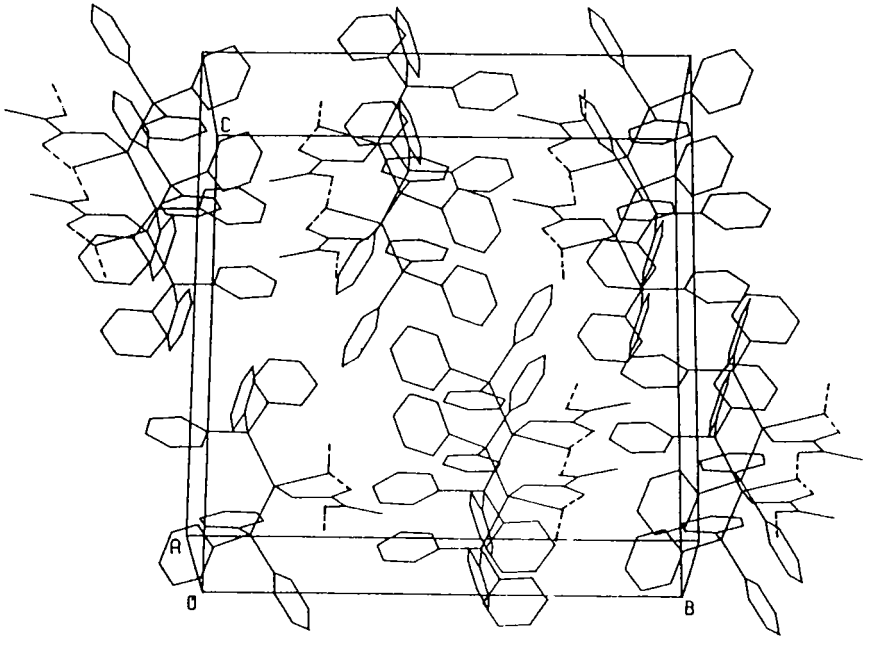


Figure 2. Packing diagram viewed down the *a* axis.

Table IV. Atomic Coordinates and Equivalent Temperature Factors (Å^2) for Non-H Atoms in $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$

Atom	x	y	z	B_{eq}
Br	0.9628(2)	0.24085(9)	0.2561(1)	4.3(1)
Cu	0.8230(2)	0.1331(1)	0.2513(1)	2.9(1)
S(1)	0.5829(4)	0.1574(2)	0.2578(2)	3.7(2)
S(2)	0.3514(5)	0.3454(3)	0.2513(3)	6.7(3)
P(1)	0.8804(4)	0.0792(2)	0.3529(2)	2.7(2)
P(2)	0.8632(4)	0.0871(2)	0.1469(2)	2.8(2)
N(1)	0.637(1)	0.2897(7)	0.2661(8)	5.2(8)
N(2)	0.307(1)	0.2147(7)	0.2801(7)	4.0(7)
C(1)	0.547(1)	0.2417(9)	0.2644(7)	3.2(8)
C(2)	0.391(2)	0.2652(9)	0.2655(7)	3.5(9)
C(11)	0.812(2)	0.1217(8)	0.4276(8)	3.2(8)
C(12)	0.778(2)	0.0867(8)	0.4859(8)	4(1)
C(13)	0.725(2)	0.122(1)	0.541(1)	6(1)
C(14)	0.703(2)	0.189(1)	0.537(1)	7(1)
C(15)	0.734(2)	0.225(1)	0.479(1)	6(1)
C(16)	0.784(2)	0.1922(8)	0.4247(8)	3.8(9)
C(21)	0.825(2)	-0.0095(8)	0.3631(7)	3.1(9)
C(22)	0.681(2)	-0.024(1)	0.3519(8)	4(1)
C(23)	0.632(2)	-0.092(1)	0.360(1)	5(1)
C(24)	0.720(2)	-0.1428(9)	0.3753(9)	5(1)
C(25)	0.864(2)	-0.130(1)	0.3856(9)	5(1)
C(26)	0.913(2)	-0.0625(9)	0.3806(8)	4(1)
C(31)	1.067(1)	0.0759(6)	0.3708(8)	2.1(7)
C(32)	1.131(2)	0.1001(9)	0.4310(8)	4(1)
C(33)	1.274(2)	0.096(1)	0.4429(9)	5(1)
C(34)	1.353(2)	0.071(1)	0.395(1)	5(1)
C(35)	1.298(2)	0.045(1)	0.335(1)	5(1)
C(36)	1.154(2)	0.0489(8)	0.3226(8)	3.4(9)
C(41)	1.049(2)	0.0656(8)	0.1368(7)	2.8(8)
C(42)	1.096(2)	0.0002(9)	0.1298(9)	4(1)
C(43)	1.240(2)	-0.013(1)	0.1296(9)	5(1)
C(44)	1.331(2)	0.040(1)	0.131(1)	6(1)
C(45)	1.284(2)	0.106(1)	0.1378(9)	4(1)
C(46)	1.140(2)	0.1189(8)	0.1392(8)	3.6(9)
C(51)	0.767(1)	0.0083(7)	0.1266(8)	2.5(8)
C(52)	0.717(2)	-0.0283(9)	0.1812(8)	4(1)
C(53)	0.638(2)	-0.0869(9)	0.1687(9)	4(1)
C(54)	0.611(2)	-0.1117(8)	0.103(1)	5(1)
C(55)	0.658(3)	-0.073(1)	0.053(1)	7(1)
C(56)	0.738(2)	-0.016(1)	0.062(1)	6(1)
C(61)	0.817(2)	0.1406(8)	0.0727(8)	2.9(8)
C(62)	0.897(2)	0.148(1)	0.018(1)	5(1)
C(63)	0.854(2)	0.187(1)	-0.038(1)	6(1)
C(64)	0.728(3)	0.216(1)	-0.042(1)	6(1)
C(65)	0.642(2)	0.211(1)	0.013(1)	7(1)
C(66)	0.690(2)	0.170(1)	0.069(1)	5(1)

* $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i^*\mathbf{a}_j^*\mathbf{a}_i\mathbf{a}_j$

atmosphere. The solution obtained by extracting the product with CH_2Cl_2 (40 mL) was layered with 2-propanol (10 mL). Crystals of *(4)* appeared several days later.

Reaction of $(Ph_3P)_2MLX$ with $(Et_4N)_2MoS_4$ or $(Et_4N)_2WS_4$.

The reaction of $(Ph_3P)_2Ag(C_2H_4N_2S_2)Cl$ *(2)* and $(Et_4N)_2MoS_4$ is given as an example. *(2)* (0.79 g, 1 mmol) and $(Et_4N)_2MoS_4$ (0.23 g, 0.5 mmol) were dissolved in CH_2Cl_2 (20 mL). After stirring for one hour, the mixture was filtered. Red plate-like crystals were produced from the filtrate after a few days. IR and elemental analyses show that it is $(Ph_3P)_3Ag_2MoS_4$. Other reactions under similar conditions as above also gave products with the compositions of $(Ph_3P)_3M_2M'S_4$, where M = Cu, Ag and M' = Mo, W.

X-ray Crystal Structure Determination of $(Ph_3P)_2Cu(C_2H_4N_2S_2)Br$ (1)

Diffraction measurements were made on a Enraf-Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation (λ = 0.71073 Å). A selected crystal with the dimension of 0.22 × 0.20 × 0.18 mm was stuck to the end of a glass fibre by neutral jelly and scanned. The unit cell parameters were determined and refined by setting the angles of 25 intense reflections ($10.98 < \theta < 11.65°$) and least-squares fit unit cell constants and orientation matrix. The following unit cell parameters were obtained: monoclinic, space group $P2_1/n$ (#14), a = 9.574(5), b = 19.422(6), c = 19.610(4) Å, β = 92.35(4)°, V = 3644(3) Å^3, Z = 4, D_c = 1.44 g/cm^3, $F(000)$ = 1608, μ_c = 19.11 cm^{-1}.

The data collection was performed by the $\omega/2\theta$ scan method within the range of $2\theta < 50°$. The scan speed was lower than 4.12 °/min and scan width was 0.55 + 0.35 tanθ (°) (in ω). The reflection data were corrected for Lp factors and empirical absorption correction. A total of 7042 reflections was collected[14], of which 2272 with $I > 2.5\sigma(I)$ were treated as significant. The structure was solved by the direct method MITHRIL and refined by full-matrix least-squares techniques[15]. Anisotropic temperature factors were applied for all non-H atoms. H atoms were positioned geometrically and not refined. The last least-squares cycle yielded the agreement factors of R = 0.071 and R_w = 0.073 ($W = 1/\sigma^2(F)$). Goodness of fit: 1.29, $(\Delta/\sigma)_{max}$ = - 0.185, residual extrema in final difference map: max ($\Delta\rho$) = 0.259, min ($\Delta\rho$) = - 0.206 e Å^{-3}.

All calculations were performed on a Micro-VAX3100 computer using the TEXSAN package[16]. Atomic coordinates and thermal parameters are listed in Table IV.

SUPPLEMENTARY MATERIALS AVAILABLE

Full lists of atomic positions and thermal parameters, bond distances and angles, observed and calculated structure factors are available from the authors upon request.

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