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Crystal Structures of Three Thiourea (tu) Complexes of Pt(II): *trans*-$[(tu)_2Pt(NH_3)_2]Cl_2$, *trans*-$[(tu)_2Pt(CH_3NH_2)_2]Cl_2\cdot 3H_2O$ and $[Pt(tu)_4]Cl_2$

JORMA ARPALAHTI, BERNHARD LIPPERT

Institut für Anorganische und Analytische Chemie, Universität Freiburg, D-7800 Freiburg, F.R.G.

HELMUT SCHÖLLHORN and ULF THEWALT

Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, D-7900 Ulm, F.R.G.

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Abstract

The structures of three Pt(II) thiourea complexes, *trans*-$[(tu)_2Pt(NH_3)_2]Cl_2$ (**1**), *trans*-$[(tu)_2Pt(CH_3NH_2)_2]Cl_2\cdot 3H_2O$ (**2**) and $[Pt(tu)_4]Cl_2$ (**3**), have been determined by X-ray diffraction and refined to $R = 0.049$ for 1026 reflections (**1**), $R = 0.057$ for 2547 reflections (**2**) and $R = 0.046$ for 2792 reflections (**3**). All the compounds crystallize in the space group $P2_1/c$ and have cell dimensions: $a = 5.437(1)$, $b = 6.450(1)$, $c = 17.980(3)$ Å, $\beta = 96.05(2)°$, $Z = 2$ (compound **1**); $a = 9.225(1)$, $b = 15.404(2)$, $c = 12.601(2)$ Å, $\beta = 105.39(2)°$, $Z = 4$ (compound **2**); and $a = 9.051(6)$, $b = 10.203(6)$, $c = 18.263(8)$ Å, $\beta = 91.12(8)°$, $Z = 4$ (compound **3**). The unit cell of **1** and **3** contains only a single type of cation, while that of **2** is formed from two independent cations. In **1** and **2** the coordination spheres of the Pt atoms are rather similar, with angles close to 90° and coplanarity of the metal and respective donor atoms. Instead, in **3** the four sulfur atoms, which surround the Pt, display a slight distortion (0.06 Å from the mean plane) towards tetrahedral.

Introduction

The general interest in the properties of square-planar Pt(II) compounds of the type $Pt(A)_2X_2$ (A = amine or ammonia, X = monovalent anion) has considerably increased after the discovery of the anticarcinogenic activity of *cis*-$Pt(NH_3)_2Cl_2$ [1]. In most cases only the *cis*-isomer shows antitumor activity, whereas the corresponding *trans*-isomer is more toxic and far less active. Since the synthesis of $Pt(A)_2X_2$ may result in mixtures of *cis*- and *trans*-isomers, the geometry of an unknown $Pt(A)_2X_2$ should always be confirmed. The efficient reactions of these Pt(II) compounds with sulfur-containing ligands such as thiourea offer a convenient way to distinguish the *cis*-isomer from the corresponding *trans*-isomer [2]. Because of the strong *trans*-labilizing effect of sulfur ligand, *cis*-$Pt(A)_2X_2$ yields $[Pt(tu)_4]X_2$ with thiourea, whereas in *trans*-$Pt(A)_2X_2$ only the labile X^--ligands are replaced to yield *trans*-$[(tu)_2Pt(A)_2]X_2$. In the last compound the remaining amine ligands are only very slowly displaced by thiourea, which makes this procedure suitable for analytical detection of both isomers [3, 4]. Thiourea has also been demonstrated to restore the biological activity of platinated DNA through reversal of cross-links induced by Pt(II) compounds [5], as also observed in model studies [6]. It has also been applied as a rescue agent in studies aimed at a reduction of acute Pt toxicity [7].

The compounds *trans*-$[(tu)_2Pt(NH_3)_2]Cl_2$ and $[Pt(tu)_4]Cl_2$ have previously been characterized by spectroscopic methods including ^1H, ^{13}C and ^{195}Pt NMR [3]. Here we wish to extend the general characterization of these simple Pt(II) coordination compounds by reporting the molecular structures of *trans*-$[(tu)_2Pt(NH_3)_2]Cl_2$ (**1**), *trans*$[(tu)_2Pt(CH_3NH_2)_2]Cl_2\cdot 3H_2O$ (**2**) and $[Pt(tu)_4]Cl_2$ (**3**).

Experimental

Thioruea (analytical grade from Riedel-De-Haen) was crystallized from methanol. K_2PtCl_4 (Degussa) was used as received. *trans*-$Pt(A)_2Cl_2$ (where A = NH_3 or NH_2CH_3) were prepared by known methods [8] and their purity was checked as previously described [4]. The compounds **1** and **3** were prepared from *trans*-$Pt(NH_3)_2Cl_2$ and K_2PtCl_4, respectively, by known methods [8]. The employment of an analogous method for the preparation of **2** from the corresponding diamine compound gave 150 mg (85%) of **2** as a colorless product. For **1** and **3**, crystals suitable for X-ray measurements were obtained by crystallization from water. In the case of **2**, 125 mg of the compound was dissolved in 1 ml water. The addition of 1 ml of 2 mol dm^{-3} HCl to the solution gave suitable crystals upon cooling in a refrigerator. The compound **2** crystallizes with three molecules of water which are, however, readily

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TABLE I. Crystallographic Data for *trans*-$[(tu)_2Pt(NH_3)_2]Cl_2$ (**1**), *trans*-$[(tu)_2Pt(CH_3NH_2)_2]Cl_2$ (**2**) and $[Pt(tu)_4]Cl_2$ (**3**)

	Compound		
	1	**2**	**3**
Formula weight	452.30	534	570.48
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	5.437(1)	9.225(1)	9.051(6)
b (Å)	6.450(1)	15.404(2)	10.203(6)
c (Å)	17.980(3)	12.601(2)	18.263(8)
β (deg)	96.05(2)	105.39(2)	91.12(8)
V (Å^3)	627.02	1726.4	1686.22
Z	2	4	4
d_{calc} (g cm^{-3})	2.396	2.056	2.247
Crystal size	0.1, 0.1, 0.2	0.2, 0.2, 0.2	0.2, 0.2, 0.6
μ (cm^{-1})	114.5	83.3	87.6
θ range (deg)	2–25	2–25	2–25
No. unique refl.	1101	3024	2803
No. refl. used in the calculations	1026^a	2547^a	2792^a
No. parameters refined	61	166	172
R	0.037	0.049	0.040
$R_w(F)$	0.049^b	0.057^c	0.046^d

$^aF_o > 2\sigma F_o$. $^bw^{-1} = \sigma^2(F) + 0.008F^2$. $^cw^{-1} = \sigma^2(F) + 0.0009F^2$. $^dw^{-1} = \sigma^2(F) + 0.005F^2$.

TABLE II. Atomic Parameters and Equivalent Isotropic Thermal Factors for *trans*-$[(tu)_2Pt(NH_3)_2]Cl_2$ (**1**)

Atom	x	y	z	U
Pt1	0.5000(0)	0.5000(0)	0.5000(0)	0.018(1)
N10	0.7027(11)	0.7646(9)	0.5245(4)	0.027(2)
S1	0.7958(3)	0.3010(3)	0.5682(1)	0.028(1)
C1	0.7514(13)	0.3207(10)	0.6613(4)	0.026(2)
N1	0.5827(16)	0.4383(14)	0.6873(4)	0.037(2)
N2	0.9013(13)	0.2078(11)	0.7091(3)	0.037(2)
Cl1	0.7379(3)	0.3762(3)	0.8669(1)	0.031(1)

TABLE III. Atomic Parameters and Equivalent Isotropic Thermal Factors for *trans*-$[(tu)_2Pt(CH_3NH_2)_2]Cl_2 \cdot 3H_2$ (**2**)

Atom	x	y	z	U
Pt1	0.0000(0)	0.5000(0)	0.5000(0)	0.020(1)
N10	0.1061(8)	0.6073(5)	0.5826(6)	0.030(2)
C10	0.1522(12)	0.6717(6)	0.5079(9)	0.043(4)
S11	0.2235(2)	0.4243(1)	0.5618(1)	0.027(1)
C11	0.3195(9)	0.4222(5)	0.4594(7)	0.024(3)
N11	0.2613(8)	0.4548(5)	0.3593(6)	0.030(2)
N12	0.4498(9)	0.3834(6)	0.4848(6)	0.035(3)
Pt2	0.50000(0)	0.0000(0)	0.5000(0)	0.021(1)
N20	0.3810(8)	0.0764(5)	0.3714(6)	0.031(2)
C20	0.3916(12)	0.1724(7)	0.4021(10)	0.054(4)
S21	0.2908(2)	−0.0193(1)	0.5653(2)	0.028(1)
C21	0.1725(9)	−0.0901(5)	0.4747(7)	0.022(2)
N21	0.0399(8)	−0.1072(5)	0.4952(6)	0.029(2)
N22	0.2095(8)	−0.1270(5)	0.3902(6)	0.031(2)
Cl1	0.0148(2)	0.4268(1)	0.7685(2)	0.039(1)
Cl2	0.4619(2)	0.6280(1)	0.7493(2)	0.037(1)
O1	0.2202(7)	0.2879(4)	0.1409(5)	0.043(2)
O2	0.0163(7)	0.2232(4)	0.7739(6)	0.044(2)
O3	0.3852(11)	0.8260(6)	0.7988(7)	0.080(4)

lost on exposure to air, as deduced by the loss of transparency. The elemental analysis was therefore made from the dried substance. *Anal.* Calc. for $C_2H_{14}N_6Cl_2PtS_2$ (**1**): C, 5.31; H, 3.12; N, 18.58; Cl, 15.68; S, 14.18. Found: C, 5.36; H, 3.05; N, 18.42; Cl, 15.94; S, 14.16. Calc. for $C_4H_{18}N_6Cl_2PtS_2$ (**2**): C, 10.00; H, 3.78; N, 17.50; S, 13.35. Found: C, 10.03; H, 3.71; N, 17.24; S, 13.38. Calc. for $C_4H_{16}N_8Cl_2PtS_4$ (**3**): C, 8.42; H, 2.83; N, 19.64; Cl, 12.43; S, 22.48. Found: C, 8.43; H, 2.73; N, 19.45; Cl, 12.67; S, 22.30%.

The crystallographic data are listed in Table I and the atomic parameters and equivalent isotropic temperature factors for **1**–**3** are given in Tables II–IV. The X-ray measurements for the three compounds were carried out at room temperature on a Philips PW 1100 single-crystal diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The reflections for **1**, **2** and **3** were collected in the $\theta/2\theta$ mode. Lp and, at a later stage, empirical absorption corrections (Program DIFABS [9]) were applied. The positions of the platinum atoms in all three structures were determined from a Patterson map. The other non-hydrogen atoms were located by subsequent ΔF-syntheses. Hydrogen atoms were ignored during the structure determinations. Complex scattering factors were taken from refs. 10 and 11. The calculations were performed on a Mikro-Vax II computer using the SHELX program system [12].

Results and Discussion

Figure 1 depicts the molecular cation of **1**; Fig. 2 shows one of the two independent cations of **2**. Molecular distances and angles of **1** and **2** are listed in Table V. The coordination spheres of the Pt atoms in both centrosymmetric compounds are rather similar, with angles close to 90° and coplanarity of the metals and the respective donor atoms. The Pt–S distances (2.307(2) Å in **1**, 2.309(2) Å and 2.317(2) Å in **2**) are significantly longer (*ca.* 35–40 σ[*]) than the Pt–N distances (2.054(6) Å in **1**, 2.057(7) Å and 2.067(7) Å in **2**). The latter are virtually

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[*] $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$.

TABLE IV. Atomic Parameters and Equivalent Isotropic Thermal Factors for $[Pt(tu)_4]Cl_2$ (3)

Atom	x	y	z	U
Pt1	0.2485(1)	0.4100(1)	0.5928(1)	0.018(1)
S10	0.1731(2)	0.4281(2)	0.7137(1)	0.028(1)
C10	−0.0176(7)	0.4568(7)	0.7085(3)	0.023(2)
N10	−0.0994(9)	0.4069(6)	0.6554(4)	0.038(2)
N11	−0.0771(7)	0.5300(8)	0.7597(4)	0.042(2)
S20	0.3275(2)	0.4109(1)	0.4729(1)	0.028(1)
C20	0.2630(7)	0.2740(7)	0.4259(4)	0.026(2)
N20	0.2983(8)	0.2685(6)	0.3550(3)	0.040(2)
N21	0.1842(8)	0.1826(6)	0.4564(3)	0.036(2)
S30	0.3323(2)	0.2024(1)	0.6273(1)	0.028(1)
C30	0.5198(8)	0.1834(6)	0.6093(4)	0.026(2)
N30	0.5892(9)	0.0875(7)	0.6443(5)	0.048(3)
N31	0.5900(7)	0.2557(6)	0.5614(3)	0.033(2)
S40	0.1498(2)	0.6125(1)	0.5614(1)	0.030(1)
C40	0.2347(8)	0.7308(7)	0.6120(4)	0.029(2)
N40	0.2016(9)	0.8558(7)	0.5931(4)	0.046(2)
N41	0.3337(10)	0.7128(7)	0.6659(4)	0.048(2)
Cl1	−0.0723(2)	0.1112(1)	0.5829(1)	0.027(1)
Cl2	0.5747(2)	0.0415(2)	0.2246(1)	0.032(1)

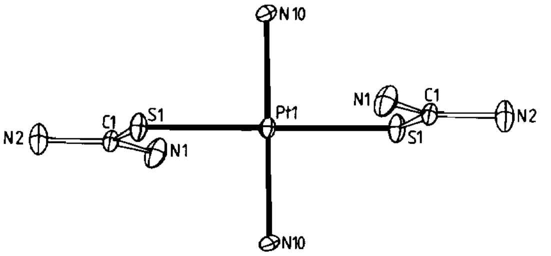

Fig. 1. The molecular cation of *trans*-$[(tu)_2Pt(NH_3)_2]Cl_2$ (1).

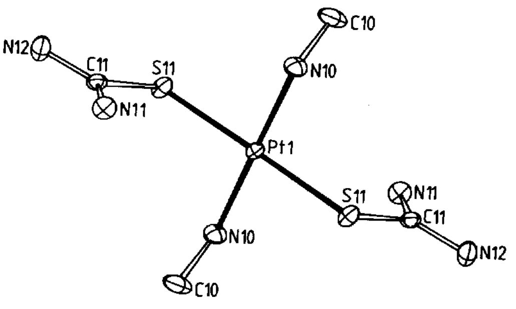

Fig. 2. One of the two independent cations of *trans*-$[(tu)_2Pt(CH_3NH_2)_2]Cl_2 \cdot 3H_2O$ (2).

TABLE V. Interatomic Distances (Å) and Angles (deg) of 1 and 2

Compound 1			
Pt1–N10	2.054(6)	N10–Pt1–S1	91.1(2)
Pt1–S1	2.307(2)	Pt1–S1–C1	108.4(3)
S1–C1	1.720(8)	S1–C1–N1	124.3(6)
C1–N1	1.314(12)	S1–C1–N2	116.6(6)
C1–N2	1.337(10)	N1–C1–N2	119.1(7)
Compound 2			
Pt1–N10	2.057(7)	Pt2–N20	2.067(7)
N10–C10	1.504(13)	N20–C20	1.526(13)
Pt1–S11	2.317(2)	Pt2–S21	2.309(2)
S11–C11	1.748(9)	S21–C21	1.738(8)
C11–N11	1.332(11)	C21–N21	1.342(11)
C11–N12	1.304(11)	C21–N22	1.329(11)
N10–Pt1–S11	88.5(2)	N20–Pt2–S21	91.9(2)
Pt1–N10–C10	112.9(6)	Pt2–N20–C20	111.6(6)
Pt1–S11–C11	110.0(3)	Pt2–S21–C21	106.6(3)
S11–C11–N11	122.4(6)	S21–C21–N21	116.2(7)
S11–C11–N12	116.2(7)	S21–C21–N22	123.0(7)
N11–C11–N12	121.3(7)	N21–C21–N22	120.8(8)

TABLE VI. Close Contacts (<3.4 Å) in 1 and 2

Compound 1^a			
N1–Cl1	3.28	C1–N1–Cl1	99
N2–Cl1	3.25	C1–N2–Cl1	100
N2–Cl1^1	3.30	Pt1–N2–Cl1^1	116
Compound 2^b			
Cl1–O2	3.14		
Cl2–O3	3.23		
N22–O2^1	2.92	C21–N22–O2^1	120
N11–Cl1^2	3.12	C11–N11–Cl1^2	139
N12–Cl2^3	3.27	C11–N12–Cl2^3	104
O1–Cl2^3	3.17		
N21–O1^4	3.02	C21–N21–O1^4	129
N21–Cl1^5	3.19	C21–N21–Cl1^5	122
N10–O2^6	2.97	Pt1–N10–O2^6	126
N12–O3^7	2.89	C11–N12–O3^7	126
N20–Cl1^8	3.28	Pt2–N20–Cl1^8	125
N22–Cl2^8	3.28	C21–N22–Cl2^8	144
O1–O2^8	2.84		

^{a}Symmetry operations: ^{1} $2 - x, -0.5 + y, 1.5 - z$. ^{b}Symmetry operations: ^{1} $-x, -y, 1 - z$, ^{2} $-x, 1 - y, 1 - z$, ^{3} $1 - x, 1 - y, 1 - z$, ^{4} $-x, -0.5 + y, 0.5 - z$, ^{5} $-x, -0.5 + y, 1.5 - z$, ^{6} $-x, -0.5 + y, 1.5 - z$, ^{7} $1 - x, -0.5 + y, 1.5 - z$, ^{8} $x, 0.5 - y, -0.5 + z$.

identical to those found in *trans*-$Pt(NH_3)_2Cl_2$ [13] and close to those of the related *trans*-$Pt(NH_3)_2L_1L_2$ (L = nucleobase) complexes [14]. Pt–S bonding is through a lone-pair of an sp^2-hybridized sulfur (*cf.* angles at S 107–110°, Pt virtually coplanar with the tu ligand as far as heavy atoms are concerned). Pt–S distance in 1 and in 2 are, although substantially longer than in Me_2SO complexes [15], in the normal range of other S-donor ligands such as pyrimidine-2-thione and thiouracil [16] or thiocarbamate [17], for example.

The tu ligands in 1 and 2 are at a substantial angle to the Pt coordination plane [dihedral angles of 99.9° (1) and 99.7° and 105.7° (2)]. As to changes in tu ligand geometry [18] as a consequence of Pt binding, alterations in bond lengths as suggested by IR spectroscopy – lengthening of S–C and shortening of

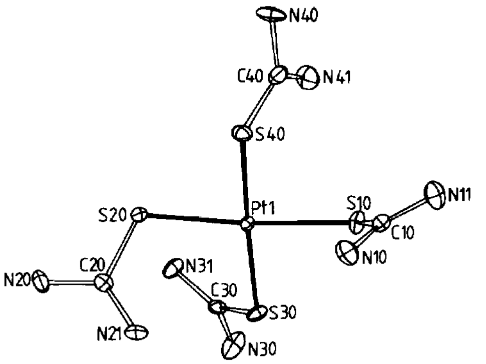

Fig. 3. The molecular cation of $[Pt(tu)_4]Cl_2$ (**3**).

TABLE VII. Interatomic Distances (Å) and Angles (deg) of **3**

Pt1–S10	2.331(2)	S10–Pt1–S20	175.2(1)
Pt1–S20	2.316(2)	S10–Pt1–S30	85.2(1)
Pt1–S30	2.333(2)	S10–Pt1–S40	92.6(1)
Pt1–S40	2.319(2)	S20–Pt1–S30	98.9(1)
S10–C10	1.751(7)	S20–Pt1–S40	83.5(1)
C10–N10	1.311(11)	S30–Pt1–S40	176.1(1)
C10–N11	1.320(11)	Pt1–S10–C10	105.6(3)
S20–C20	1.734(8)	Pt1–S20–C20	111.0(3)
C20–N20	1.341(11)	Pt1–S30–C30	111.2(3)
C20–N21	1.306(10)	Pt1–S40–C40	109.3(3)
S30–C30	1.745(8)	S10–C10–N10	121.2(6)
C30–N30	1.321(11)	S10–C10–N11	118.1(6)
C30–N31	1.317(10)	N10–C10–N11	120.7(7)
S40–C40	1.696(8)	S20–C20–N20	115.3(6)
C40–N40	1.253(11)	S20–C20–N21	123.0(6)
C40–N41	1.331(12)	N20–C20–N21	121.6(6)
		S30–C30–N30	116.5(6)
		S30–C30–N31	123.1(6)
		N30–C30–N31	120.3(7)
		S40–C40–N40	115.9(7)
		S40–C40–N41	126.6(6)
		N40–C40–N41	117.5(7)

C–N bonds [19] – are too small to be detected by X-ray crystallography. On the other hand, the S–C–N angles are affected in such a way that the angle with N close to the metal becomes larger by *ca.* 3–4°, while the other S–C–N angle decreases to the same extent. Similar changes have been observed in other metal tu complexes [20, 21].

In Table VI, close contacts (<3.4 Å) in the crystal lattices of **1** and **2** are given. In **1**, each of the two Cl^- anions is hydrogen bonded to two NH_2 groups of a tu ligand and, in addition, forms an intermolecular H bond to the NH_2 of a tu ligand of an adjacent cation. Hydrogen bonding is more complicated in **2**. The amino groups of the tu ligands not only form H bonds with chloride anions but also with water molecules. In contrast to **1**, the amino groups of the CH_3NH_2 groups are also involved in H bonding (with Cl^- and OH_2, respectively). Finally, there is H bonding between Cl^- and H_2O, and between H_2O molecules. As expected, the H bonding schemes of the two independent molecules of **2** are different.

TABLE VIII. Close Contacts (<3.4 Å) in **3**^{a}

N10–Cl1	3.31	C10–N10–Cl1	127
N21–Cl1	3.39	C20–N21–Cl1	146
N30–Cl1^1	3.29	C30–N30–Cl1^1	103
N21–Cl1^2	3.24	C20–N20–Cl1^2	138
N30–Cl2^3	3.13	C30–N30–Cl2^3	117
N41–Cl2^4	3.30	C40–N41–Cl2^4	120
N11–Cl1^5	3.26	C10–N11–Cl1^5	127
N20–Cl2^6	3.36	C20–N20–Cl2^6	118
N10–Cl2^7	3.27	C10–N10–Cl2^7	99
N11–Cl2^7	3.29	C10–N11–Cl2^7	98

^{a}Symmetry operations: $^1\,x-1, y, z$, $^2\,-x, -y, 1-z$, $^3\,1-x, -y, -y, 1-z$, $^4\,1-x, 1-y, 1-z$, $^5\,-x, 0.5+y, 1.5-z$, $^6\,1-x, 0.5-y, 0.5-z$, $^7\,-1+x, 0.5-y, 0.5+z$.

In Fig. 3, the molecular cation of $[Pt(tu)_4]Cl_2$ (**3**) is shown. Selected bond lengths and angles are given in Table VII. The Pt is surrounded by four sulfur donors which display a slight distortion from square-planar towards tetrahedral: S atoms *trans* to each other are 0.06 Å either above or below the mean plane. The distortion is comparable to that observed with $[Pd(tu)_4]Cl_2$ [20], or $[Pt(bipy)_2](NO_3)_2\cdot H_2O$ [22], yet clearly smaller than in $[Pt(PEt_3)_4](ClO_4)_2$ [23], where the phosphorus atoms deviate as much as 0.6 Å from the mean plane. The tu ligands are arranged in such a way that two *trans*-positioned tu groups are at the same side of the Pt coordination plane, on the opposite side to the two others. Thus, the geometry of **3** is different from the orthorhombic form of the corresponding Pd complex, in which the tu ligands are arranged such that the cation is roughly centrosymmetrical [20]. Details of the geometry of the tu ligands in **3** do not differ significantly from those in **1** and **2**. As shown in Table VIII, there is extensive hydrogen bonding between the NH_2 groups of the tu ligands and the Cl^- counterions. Four of the eight NH_2 groups (N10, N11, N21, N30) form two H bonds each, two (N20, N41) form a single H bond with Cl^-, while two (N31, N40) do not participate in H bonding.

Supplementary Material

Tables of anisotropic thermal parameters, torsion angles, and observed and calculated structure factors can be obtained from the authors on request.

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