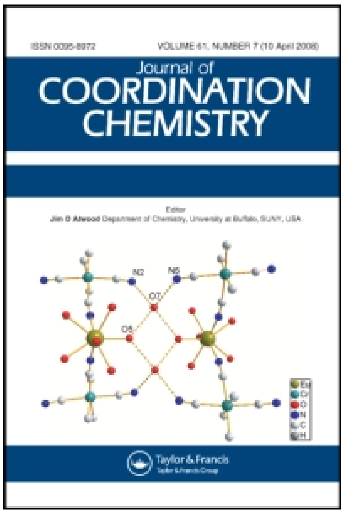

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Synthesis and Crystal Structure of a One-Dimensional Thiocyanate-Bridged Heterometallic Complex of Copper(II) and Silver(I)

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SYNTHESIS AND CRYSTAL STRUCTURE OF A ONE-DIMENSIONAL THIOCYANATE-BRIDGED HETEROMETALLIC COMPLEX OF COPPER(II) AND SILVER(I)

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The title polymeric complex of Cu(II) and Ag(I) bridged by thiocyanate, $[\{Cu_2(nelin)_2Ag_2(SCN)_5\}_n](SCN)_n$ (nelin = 1,9-diamino-5-methyl-5-nitro-3,7-diazanonane), has been prepared and its structure determined by X-ray diffraction methods. The complex crystallizes in space group $P\bar{1}$ with $a = 11.371(2)$, $b = 13.594(2)$, $c = 15.232(3)$ Å, $\alpha = 68.50(1)$, $\beta = 69.18(1)$, $\gamma = 87.03(1)°$. The Cu(II) atom is square-pyramidal, formed by one SCN^- anion and one nelin ligand, while the Ag(I) atom is a tetrahedral, formed by four SCN^- anions. Three different thiocyanate anions exist in the complex. Both 1,3-μ-SCN^- and 1,1,3-μ-SCN^- act as bridge ligands, linking Ag(I), Ag(I) atoms and Cu(II), Ag(I) atoms to form the one-dimensional polymeric structure. The coordination distance between Ag(I) and S of 1,1,3-μ-SCN^- anion is apparently longer than that between Ag(I) and S of 1,3-μ-SCN^- anion.

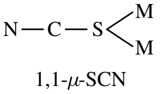
Keywords: Copper(II); Silver(I); Crystal structure; Thiocyanate; Polymeric complex

INTRODUCTION

The *pseudo*-halide SCN^- is known to coordinate to metals in both terminal and bridging modes. As bridging ligand the thiocyanate anion can link a pair of metal centers in either end-to-end (1,3-μ-SCN) or end-on (1,1-μ-SCN,1,1-μ-NCS) configuration. The thiocyanate anion may link a third or even a fourth metal atom to give rise to a 1,1,3-μ-SCN or 1,1,1,3-μ-SCN mode:

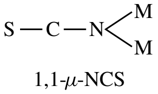
$$M—N—C—S—M$$

1,3-μ-NCS



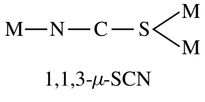
$$N—C—S\begin{matrix}M\\M\end{matrix}$$

1,1-μ-SCN



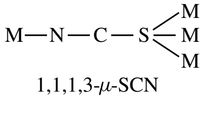
$$S—C—N\begin{matrix}M\\M\end{matrix}$$

1,1-μ-NCS



$$M—N—C—S\begin{matrix}M\\M\end{matrix}$$

1,1,3-μ-SCN



$$M—N—C—S\begin{matrix}M\\M\\M\end{matrix}$$

1,1,1,3-μ-SCN

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Polynuclear copper or nickel thiocyanate systems are of interest due to the broad range of their structural and magnetic properties [1–3]. However, the vast majority of studies have focused on homonuclear thiocyanate complexes. Reports on heteronuclear thiocyanate complexes are relatively few [4–6]. As a part of our research on heteronuclear thiocyanate complexes, we report the synthesis and crystal structure of the title heteronuclear complex of Cu(II) and Ag(I).

EXPERIMENTAL

Preparation

The starting material, $[Cu(nelin)](ClO_4)_2$, was prepared according to literature [7]. Fresh solid AgSCN (166 mg, 1 mmol), prepared through the reaction of $AgNO_3$ with equimolar KSCN in an aqueous solution, was dissolved in 10 mL aqueous solution of KSCN (200 mg, 2 mmol) with continuous stirring. The resulting solution was dropped into a 15 mL aqueous solution containing $[Cu(nelin)](ClO_4)_2$ (481 mg, 1 mmol) with stirring at room temperature. A solid was obtained and then dissolved in water at 60°C. The solution was cooled slowly to room temperature, and blue crystals of the title heterometallic polymeric complex were formed. C, H, and N analysis with an Erba 1160 instrument indicated the product to be $[\{Cu_2(nelin)_2Ag_2(SCN)_5\}_n](SCN)_n$. Anal. Calcd. for $C_{22}H_{30}N_{16}O_4S_6Ag_2Cu_2$(%): C, 23.62; H, 2.68; N, 20.04. Found: C, 23.49; H, 2.79; N, 19.93. Infrared spectra were recorded using a Nicolet 205 Spectrophotometer (4000–400 cm^{-1}) with a crystalline sample spread on KBr pellets.

Crystal Structure Determination

A single crystal with dimension $0.48 \times 0.46 \times 0.28$ mm was mounted on a glass fiber. Diffraction intensity data were collected on a Siemens P4 diffractometer up to $(2\theta)_{max}$ of 50.0° with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$Å) using the ω scan technique. A total of 7015 independent reflections were collected, among which 5177 reflections were considered as observed [$I > 2\sigma(1)$] and used for the structure refinement. Usual Lp and empirical adsorption corrections were applied.

The structure was solved by direct methods followed by Fourier synthesis. The structure was refined on F^2 by full-matrix lease-square methods. H atoms were located in a difference Fourier map. Anisotropic refinement including all nonH atoms, using the SHELXTL software package [8], converged to agreement factors $R = 0.0550$ and $Rw = 0.1652$, where $w = 1/\sigma^2(Fo^2) + (0.1010P)^2 + 1.7613P]$. The highest peak in the final difference Fourier map was $1.941 e \cdot Å^{-3}$. Atomic scattering factors used were taken from International Tables for X-ray crystallography [9].

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: $C_{22}H_{30}N_{16}O_4S_6Ag_2Cu_2$, $M = 1117.80$, triclinic, space group $P\bar{1}$, $a = 11.371(2)$, $b = 13.594(2)$, $c = 15.232(3)$Å, $\alpha = 68.50(1)$, $\beta = 69.18(1)$, $\gamma = 87.03(1)$°, $V = 2039.3(6)$ Å^3, $Z = 2$, $Dc = 1.820$ g cm^{-3}, $F(000) = 1180$, μ(Mo-Kα) $= 2.333$ mm^{-1}.

Fractional atomic coordinates and equivalent isotropic thermal parameters for all nonH atoms are listed in Table I. Selected bond distances and angles are listed in Table II.

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*U*(eq)
Ag(1)	5425(1)	9061(1)	5684(1)	65(1)
Ag(2)	9466(1)	5914(1)	4301(1)	71(1)
Cu(1)	−43(1)	8986(1)	7785(1)	44(1)
Cu(2)	15035(1)	7341(1)	1905(1)	49(1)
S(1)	3788(2)	8918(1)	4833(1)	45(1)
S(2)	4165(2)	8251(2)	7544(2)	66(1)
S(3)	7418(2)	6274(2)	5437(2)	90(1)
S(4)	10743(2)	6931(2)	2490(2)	72(1)
S(5)	11120(2)	6151(2)	5158(1)	55(1)
S(6)	−2266(4)	10077(3)	9461(3)	126(1)
O(1)	−2732(7)	5791(9)	9618(6)	130(3)
O(2)	−3468(6)	6643(6)	8549(6)	101(2)
O(3)	17882(7)	4792(9)	1351(7)	135(3)
O(4)	18451(7)	5844(8)	1815(9)	167(5)
N(1)	−86(7)	10511(5)	6882(6)	68(2)
N(2)	−1366(5)	8624(4)	7315(4)	43(1)
N(3)	−321(5)	7500(5)	8843(4)	47(1)
N(4)	1106(6)	9308(6)	8412(6)	66(2)
N(5)	−2584(6)	6385(5)	8804(5)	61(2)
N(6)	14937(6)	8700(5)	2154(7)	80(2)
N(7)	16290(5)	6970(4)	2624(4)	40(1)
N(8)	15283(5)	6038(4)	1560(4)	43(1)
N(9)	13968(6)	7753(6)	1013(6)	79(2)
N(10)	17673(6)	5295(6)	1879(6)	64(2)
N(11)	1574(5)	8644(5)	6521(5)	58(2)
N(12)	5791(8)	9008(6)	8209(7)	87(2)
N(13)	7438(5)	8503(4)	4848(4)	40(1)
N(14)	8994(6)	8247(6)	1872(6)	75(2)
N(15)	13319(6)	6524(5)	3445(5)	65(2)
N(16)	−2917(8)	7927(5)	10205(7)	113(4)
C(1)	−1164(9)	10539(6)	6564(8)	75(2)
C(2)	−1264(8)	9544(6)	6376(6)	63(2)
C(3)	−1239(6)	7633(6)	7127(5)	50(2)
C(4)	−1254(6)	6636(5)	7989(5)	48(2)
C(5)	−284(6)	6638(6)	8473(5)	51(2)
C(6)	657(7)	7415(7)	9305(6)	68(2)
C(7)	824(8)	8442(8)	9413(7)	75(3)
C(8)	−1073(8)	5680(7)	7662(7)	73(2)
C(9)	15950(8)	8755(6)	2529(7)	74(3)
C(10)	16075(7)	7669(6)	3210(6)	60(2)
C(11)	16252(7)	5845(5)	3260(5)	48(2)
C(12)	16384(6)	5059(5)	2749(5)	47(2)
C(13)	15380(6)	5027(5)	2323(5)	48(2)
C(14)	14215(7)	5923(7)	1235(6)	66(2)
C(15)	14065(8)	6982(8)	536(6)	74(3)
C(16)	16416(9)	3957(6)	3497(7)	76(3)
C(17)	2480(6)	8768(5)	5828(5)	40(1)
C(18)	5141(7)	8688(5)	7922(6)	57(2)
C(19)	7387(7)	7552(9)	5111(6)	78(3)
C(20)	9695(6)	7688(5)	2121(5)	45(2)
C(21)	12410(6)	6351(5)	4151(5)	48(2)
C(22)	−2671(6)	8820(4)	9903(5)	120(6)

TABLE II Bond distances (Å) and angles (°)

Ag(1)–S(1)	2.669(2)	Ag(1)–S(2)	2.506(2)
Ag(1)–S(1)#1	2.671(2)	Ag(1)–N(13)	2.427(5)
Ag(1)–Ag(1)#1	3.012(1)	Ag(2)–S(3)	2.510(3)
Ag(2)–S(4)	2.488(2)	Ag(2)–S(5)	2.733(2)
Ag(2)–S(5)#2	2.666(2)	Ag(2)–Ag(2)#2	3.136(1)
Cu(1)–N(1)	2.037(7)	Cu(1)–N(2)	2.030(5)
Cu(1)–N(3)	2.024(6)	Cu(1)–N(4)	2.016(6)
Cu(1)–N(11)	2.315(6)	Cu(2)–N(6)	2.007(7)
Cu(2)–N(7)	2.030(5)	Cu(2)–N(8)	2.005(6)
Cu(2)–N(9)	2.044(7)	Cu(2)–N(15)	2.367(6)
S(1)–C(17)	1.660(6)	S(2)–C(18)	1.641(8)
S(3)–C(19)	1.625(12)	S(4)–C(20)	1.649(7)
S(5)–C(21)	1.648(7)	S(6)–C(22)	1.613(4)
O(1)–N(5)	1.161(10)	O(2)–N(5)	1.195(9)
O(3)–N(10)	1.193(10)	O(4)–N(10)	1.142(9)
N(1)–C(1)	1.484(10)	N(2)–C(3)	1.469(9)
N(2)–C(2)	1.486(9)	N(3)–C(5)	1.468(9)
N(3)–C(6)	1.494(9)	N(4)–C(7)	1.479(12)
N(5)–C(4)	1.534(8)	N(6)–C(9)	1.472(12)
N(7)–C(11)	1.474(8)	N(7)–C(10)	1.484(8)
N(8)–C(13)	1.469(8)	N(8)–C(14)	1.500(8)
N(9)–C(15)	1.459(13)	N(10)–C(12)	1.537(9)
N(11)–C(17)	1.147(8)	N(12)–C(18)	1.153(10)
N(13)–C(19)	1.203(11)	N(14)–C(20)	1.139(9)
N(15)–C(21)	1.153(9)	N(16)–C(22)	1.140(4)
C(1)–C(2)	1.482(11)	C(3)–C(4)	1.498(10)
C(4)–C(5)	1.528(9)	C(4)–C(8)	1.535(10)
C(6)–C(7)	1.493(13)	C(9)–C(10)	1.496(12)
C(11)–C(12)	1.509(10)	C(12)–C(13)	1.510(9)
C(12)–C(16)	1.522(10)	C(14)–C(15)	1.488(12)
S(1)–Ag(1)–S(1)#1	111.32(5)	S(1)–Ag(1)–S(2)	103.51(6)
S(1)–Ag(1)–N(13)	109.60(13)	S(1)#1–Ag(1)–S(2)	110.29(7)
S(1)#1–Ag(1)–N(13)	97.53(12)	S(2)–Ag(1)–N(13)	124.52(14)
S(3)–Ag(2)–S(4)	130.40(8)	S(3)–Ag(2)–S(5)	102.11(9)
S(3)–Ag(2)–S(5)#2	96.86(7)	S(4)–Ag(2)–S(5)	99.32(7)
S(4)–Ag(2)–S(5)#2	117.35(8)	S(5)–Ag(2)–S(5)#2	109.00(5)
N(1)–Cu(1)–N(2)	85.4(2)	N(1)–Cu(1)–N(3)	169.5(3)
N(1)–Cu(1)–N(4)	96.7(3)	N(1)–Cu(1)–N(11)	93.7(3)
N(2)–Cu(1)–N(3)	90.8(2)	N(2)–Cu(1)–N(4)	173.3(3)
N(2)–Cu(1)–N(11)	91.7(2)	N(3)–Cu(1)–N(4)	85.9(3)
N(3)–Cu(1)–N(11)	96.2(2)	N(4)–Cu(1)–N(11)	94.6(3)
N(6)–Cu(2)–N(7)	86.0(3)	N(6)–Cu(2)–N(8)	174.9(3)
N(6)–Cu(2)–N(9)	95.8(3)	N(6)–Cu(2)–N(15)	90.6(3)
N(7)–Cu(2)–N(8)	92.6(2)	N(7)–Cu(2)–N(9)	172.6(3)
N(7)–Cu(2)–N(15)	91.6(2)	N(8)–Cu(2)–N(9)	84.9(3)
N(8)–Cu(2)–N(15)	94.4(2)	N(9)–Cu(2)–N(15)	95.5(3)
C(17)–S(1)–Ag(1)	97.1(2)	C(17)–S(1)–Ag(1)#1	100.7(2)
Ag(1)–S(1)–Ag(1)#1	68.68(5)	C(18)–S(2)–Ag(1)	96.8(3)
C(19)–S(3)–Ag(2)	108.1(3)	C(20)–S(4)–Ag(2)	101.1(2)
C(21)–S(5)–Ag(2)	96.4(3)	C(21)–S(5)–Ag(2)#2	100.2(2)
Ag(2)–S(5)–Ag(2)#2	71.00(5)	C(1)–N(1)–Cu(1)	107.6(5)
C(2)–N(2)–C(3)	110.6(5)	C(2)–N(2)–Cu(1)	105.3(4)
C(3)–N(2)–Cu(1)	115.3(4)	C(5)–N(3)–C(6)	110.7(6)
C(5)–N(3)–Cu(1)	115.4(4)	C(6)–N(3)–Cu(1)	106.7(5)
C(7)–N(4)–Cu(1)	106.8(5)	O(1)–N(5)–O(2)	120.4(7)
O(1)–N(5)–C(4)	119.3(7)	O(2)–N(5)–C(4)	118.8(7)
C(9)–N(6)–Cu(2)	107.1(4)	C(10)–N(7)–C(11)	112.1(5)
C(10)–N(7)–Cu(2)	105.4(4)	C(11)–N(7)–Cu(2)	116.6(4)
C(13)–N(8)–C(14)	109.9(5)	C(13)–N(8)–Cu(2)	119.0(4)

(*continued*)

TABLE II Continued

C(14)–N(8)–Cu(2)	106.1(4)	C(15)–N(9)–Cu(2)	109.0(5)
O(3)–N(10)–O(4)	121.0(9)	O(13)–N(10)–C(12)	117.7(8)
O(4)–N(10)–C(12)	120.7(8)	C(17)–N(11)–Cu(1)	160.5(6)
C(19)–N(13)–Ag(1)	110.7(5)	C(21)–N(15)–Cu(2)	164.9(6)
N(11)–C(17)–S(1)	178.6(6)	N(12)–C(18)–S(2)	177.6(8)
N(13)–C(19)–S(3)	176.3(7)	N(14)–C(20)–S(4)	176.9(7)
N(15)–C(21)–S(5)	177.8(7)	N(16)–C(22)–S(6)	177.9(8)

*Symmetry code. #1: $-x+1$, $-y+2$, $-z+1$; #2: $-x+2$, $-y+1$, $-z+1$.

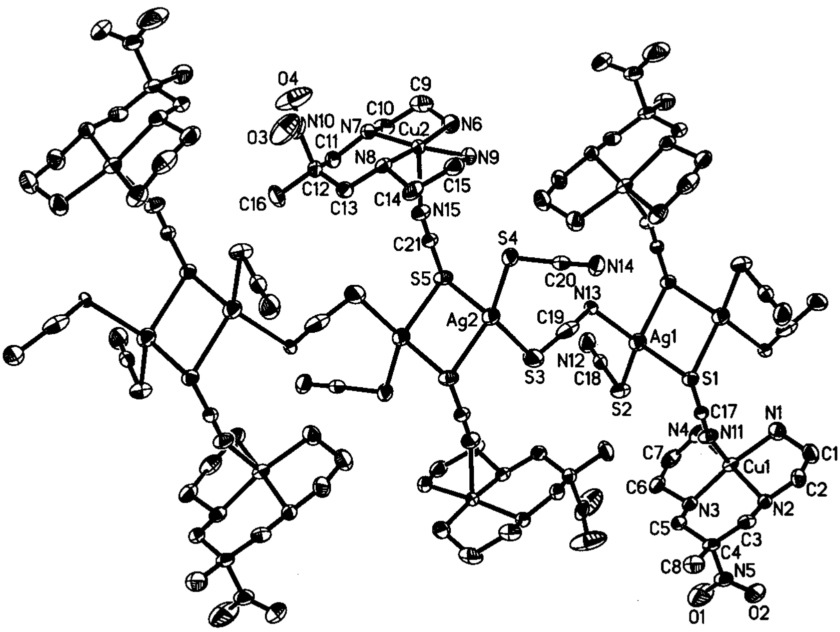

FIGURE 1 Coordination environment around Cu(II) and Ag(I) atoms showing 40% probability displacement ellipsoids. H atoms are omitted for clarity.

The perspective molecular structure is illustrated in Fig. 1, together with the numbering scheme. The coordination tetrahedron around Ag(1) formed by the one terminal S, two μ-atoms S [S(1)] from 1,1,3-μ-SCN$^-$ and one N atom from 1,3-μ-SCN$^-$, is distorted, the coordination angles ranging from 97.53(12) to 124.5(14)°. One terminal S, one S atom from 1,3-μ-SCN$^-$ and two μ-atoms S [S(5)] from 1,1,3-μ-SCN$^-$ coordinate to a Ag(2) atom with a distorted tetrahedral geometry, S–Ag–S angles varying from 96.86(7) to 130.40(8)°.

Each copper(II) atom is bound to one nitrogen atom from 1,1,3-μ-SCN ligand, which is also coordinated to Ag(I) atoms. The nitrogen atom lies in the axial position of a deformed square-pyramidal around the copper(II), the basal plane being filled with the four nitrogen atoms of the nelin ligand. The Cu–N axial distance is close to the similar bond found in other complexes [10].

Three different thiocyanate anions exist in the complex. Both 1,3-μ-SCN$^-$ and 1,1,3-μ-SCN$^-$ anions act as bridge ligands and link adjacent Ag atoms to form the one-dimensional polymeric chain along the *b* direction, meanwhile the copper(II) atoms, connected with Ag, is located on both sides of the chain. The S atom from 1,1,3-μ-SCN$^-$ links adjacent Ag atoms with Ag–Ag distances of 3.012(1) and 3.136(1) Å. The Ag–S(1,1,3-μ-SCN$^-$) distances [averages 2.685 Å] is much longer than that of Ag–S(1,3-μ-SCN$^-$) [2.510(3) Å] and of Ag–S (terminal S) [average 2.497 Å]. The C–N distance (average 1.156 Å), C–S distance (average 1.639 Å) and N–C–S angles (average 176.7°) in the SCN$^-$ moiety show the normal structure of the thiocyanate in the complex.

The crystal structure consists of polymeric molecules as shown in Fig. 2.

Infrared Spectrum

It is well-established criterion of infrared spectroscopy that ν_{as}(NCS) < 2000 cm^{-1} characterizes the SCN$^-$ anion with a μ-N bridge mode, while ν_{as}(NCS) $\geq$ 2100cm^{-1} indicated the thiocyanate bridge with a 1,3-μ or 1,1,3-μ bridge mode [11]. The strong ν_{as}(NCS) absorption peak at 2102 cm^{-1} in the complex shows the presence of 1,3-μ

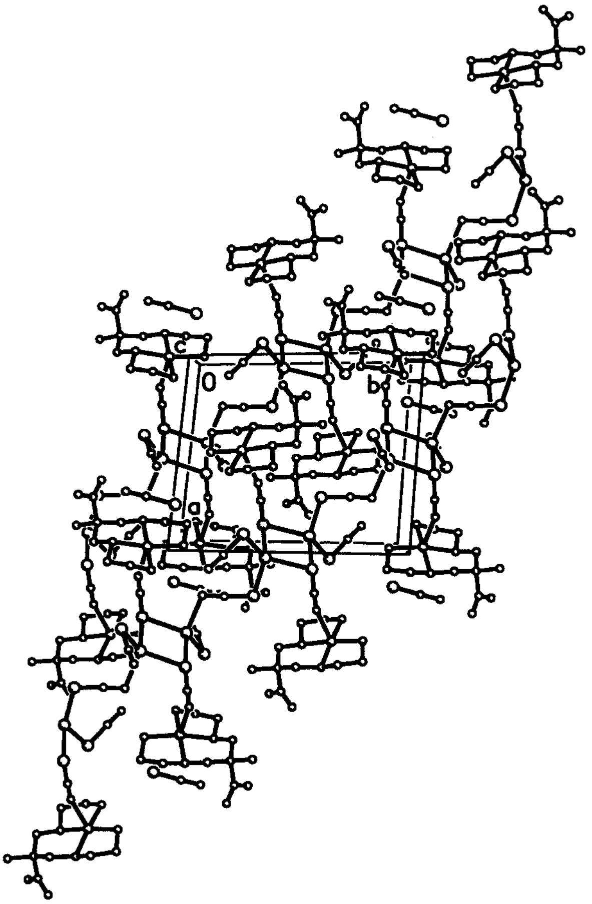

FIGURE 2 Packing diagram of the polymeric complex showing the one-dimensional chain.

or 1,1,3-μ bridge thiocyanate ligands. Another strong ν_{as}(NCS) peak at 2077 cm^{-1} shows the presence of nonbridging thiocyanates (Ag–SCN). There are two peaks, at 760(s) and 733(sh, m) cm^{-1}, which means the coordination modes of the sulfur atoms in the two bridging thiocyanate ligands are different [12]. This result agrees well with the molecular structure mentioned above.

Supplementary Material

Full lists of crystallographic data are available from the author upon request.

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