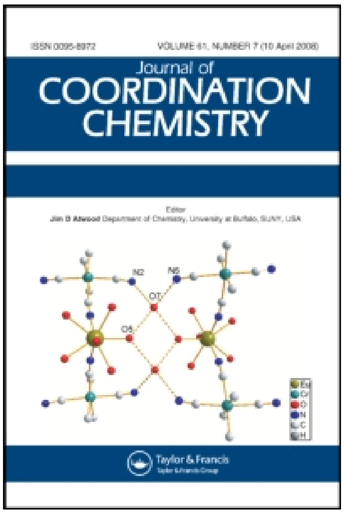

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Synthesis and Characterization of a Novel Heterotrimetallic Butterfly-Like Complex, $[(CH_3CH_2)_4N][(PPh3)_2\{AgS_3WOCu\}\{CN\}]$

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SYNTHESIS AND CHARACTERIZATION OF A NOVEL HETEROTRIMETALLIC BUTTERFLY-LIKE COMPLEX, $[(CH_3CH_2)_4N][(PPh_3)_2\{AgS_3WOCu\}\{CN\}]$

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A novel heterometallic butterfly-type complex with three different metals, $[(CH_3CH_2)_4N][(PPh_3)_2\{AgS_3WOCu\}(CN)]$, (I), has been obtained by the reaction of $[Et_4N]_2[OWS_3Cu(CN)]$ with $(PPh_3)_2AgNO_3$. The complex crystallizes in space group $P2_1/n$ with $a=20.026(5)$, $b=10.556(2)$, $c=22.713(4)$ Å, $\beta=101.39(2)°$, $U=4707$ Å^3; $Z=4$; $d_{calcd}=1.62\,\mathrm{g\,cm^{-3}}$; $\mu=35.78\,\mathrm{cm^{-1}}$; $T=296$K; $\lambda(\mathrm{Mo}K\alpha)=0.71069$ Å; $2\theta_{max}=50.1°$; final $R=0.066$ for 2967 observed reflections with $I>4\sigma(I)$ and 296 variables. In the synthesis, the fragment of the anion of the starting material (OWS_3CuCN) remains unchanged in the product. The chirality of the butterfly-type compound containing the three different metals is discussed

Keywords: Tungsten, copper, silver, sulfur, heterotrimetallic complex, X-ray structure

INTRODUCTION

The tetrathiometalate anions, MoS_4^{2-} and WS_4^{2-}, which are useful and versatile reagents, play a key role in some biological processes.[1–2] One important function is coordination.[3] Many types of compounds, which are interesting from the standpoint of structural chemistry, are formed with the aid of doubly, triply, and *quasi*-quadruply bridging tetrathiometalate ligands. The MoS_4^{2-} anion has been claimed to be the most effective antagonist[2] of copper metabolism. There has been extensive research on MoS_4^{2-}/Cu(I) and WS_4^{2-}/Cu(I) complexes,[4–9] which have shown rich structural variation. Meanwhile, a number of MoS_4^{2-}/Ag(I) and WS_4^{2-}/Ag(I) complexes[4(b),9–12] have been obtained.

Recently, some heterometallic, trinuclear incomplete cubane-like clusters, and tetranuclear cubane-like clusters, belonging to the M/Cu/S or M/Ag/S (M = Mo, or W) types, such as with the core of $\{M_3CuS_4\}^{5+}$,[8(a)–(f)] $\{M_2M'S_4\}^{3+}$ [13,14] and $\{M_2Cu_2S_4\}^{4+}$ [15] (M = Mo, or W; M′ = Cu, or Ag}, were synthesized by the unit construction method[16] from the trinuclear clusters $M_3S_4[S_2P(OCH_2CH_3)_2]_4\cdot H_2O$[17,18] and dinuclear complexes $M_2S_4(SCH_2CH_2S)_2^{2-}$,[19] in our laboratory. The unit construction method[16] is a convenient method for obtaining multimetallic complexes or clusters, using reactive fragments which contain active sulphido atoms as building blocks. To date the synthetic method has been only used to obtain bimetallic complexes. In this paper we describe the use of this method to obtain a novel trimetallic complex.

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The basal fragment of the anion $[OMS_3Cu(CN)]^{2-}$ [19] (M = Mo, or W) may be expected to combine with another metal complex to form a trinuclear complex, for example the butterfly-like $OMoS_3Cu_2(PPh_3)_3$ [20] clusters. However, no trimetallic complex so obtained has been structurally characterized, including those containing Cu and Ag. The main difficulty may be associated with statistic disorder of the Cu and Ag atoms. Herein an example is reported with the Cu and Ag positions located. As pointed out by Vahrenkamp,[21] higher nuclearity clusters with three or more different types of metals should be chiral for most compositions and framework geometries. The chirality of the butterfly-like framework geometries is discussed below.

EXPERIMENTAL

All reagents and solvents were above AR grade and were used as purchased. The complex $[Et_4N]_2[OWS_3Cu(CN)]$[9] was synthesized according to literature methods. $[AgNO_3(PPh_3)_2]$ was obtained from a CH_2Cl_2/EtOH solution of PPh_3 and $AgNO_3$ with a 2:1 mol ratio. Elemental analyses were carried out by the elemental analysis laboratories of our institute. Electronic spectra were obtained using a Shimadzu UV-3000 spectrophotometer. Infrared spectra were recorded on a Perkin Elmer 577 spectrometer.

$[(CH_3CH_2)_4N][(PPh_3)_2\{AgS_3WOCu\}(CN)]$ (I)

$[AgNO_3(PPh_3)_2]$ (0.343 g, 0.50 mmol) in 10 cm^3 of CH_2Cl_2 was added slowly to a $[Et_4N]_2(NCCuWOS_3)$ (0.32 g, 0.50 mmol) solution in 20 cm^3 of CH_3CN. After stirring for a while, 20 cm^3 of ether was added and the mixture filtered. The filtrate was allowed to stand at 3–5°C for one day, and 0.35 g (yield 62%) of yellow, needles of the complex were obtained Anal:, found: C, 46.8; H, 4.7; Ag, 8.4; Cu, 5.9; N, 3.0; P, 5.4; S, 9.1%. $C_{45}H_{50}AgCuN_2OP_2S_3W$ requires C, 47.1; H, 4.4; Ag, 9.4; Cu, 5.5; N, 2.4; P, 5.4; S, 8.4%. *IR* (KBr pellet, cm^{-1}): δC–H in PPH_3 750(vs), 700(vs); W–O 925(vs); Ag–P 515(vs), 505(vs); W–μ_2–S and W–μ_3–S 490(s), 455(vs), 426(m), 410(m); C–N of CN ligand 2120(m). Electronic spectrum (λ (ε), nm (10^{-3} M^{-1} cm^{-1}) in CH_3CN): 360 (5.11), 335 (5.65), 275 (21.8), 266 (18.2, shoulder), 258 (13.7, sh), 245 (16.7, sh), 236 (18.0). For comparison, the electronic spectrum of $[Et_4N]_2[(CN)CuS_3WO]$ in CH_3CN is 366 (5.47), 336 (6.67), 270 (10.5), 266 (10.7), 260 (9.48, sh), 235 (12.5).

Crystal Structure Determination

The crystal data for the compound are summarized in Table I, together with other experimental details. Data were collected on a RIGAKU AFC5R diffractometer using Mo*K*α radiation at 296K. Scan speed was varied on the basis of intensity. Three standard reflections were measured periodically; the absence of random deviations of intensity indicated crystal stability. The data were corrected for Lorentz and polarization factors and for absorption using empirical scan data and DIFABS.

TABLE I
Crystal Data and some experimental details for $[Et_4N][(Ph_3P)_2AgS_3WOCu(CN)]$.

Compound	I
chemical formula	$C_{45}H_{50}N_2P_2S_3OWCuAg$
formula weight	1148.3
crystal colour	yellow
crystal system	monoclinic
space group	$P2_1/n$
unit cell parameters	
a	20.026(5)Å
b	10.556(2)Å
c	22.713(2)Å
β	101.39(2)°
V	4707 Å^3
Z	4
μ	35.78 cm^{-1}
$2\theta_{max}$	50.1°
d_{calc}.	1.62 g cm^{-3}
temp.	296K
diffractometer	Rigaku AFC5R
radiation	MoKα (λ=0.71069 Å)
solution method	direct methods
correction	Lp, ψ, DIFABS
residuals: R, R_w	0.066, 0.095
goodness of fit, S	4.39
No. of unique data	9112
No. of observns with $I>4(\sigma(I))$	2967
max shift $(\Delta/\sigma)_{max}$ in final cycle	0.26
largest/smallest peaks in final diff map	1.89/−1.13e Å^{-3}
scan type	ω
max. scan speed	16° min^{-1}

The structure was solved by direct methods using *MITHRIL*[22] of the TEXSAN program package;[23] the W, Ag and Cu atoms were located in the E map. Most non-hydrogen atoms were located using the succeeding *DIRDIF* program[24] of the TEXSAN program package; some non-hydrogen atoms were located in subsequent difference Fourier syntheses. The structure was refined by the SDP program[25] using full-matrix least-squares techniques with anisotropic thermal parameters for W, Ag, Cu, S, P, O, C and N atoms in the CN ligand, and isotropic thermal parameters for all C atoms in the PPh_3 ligands. Final $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.066$, $R_w=[\Sigma(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}=0.095$ and $S=(\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{var}))^{1/2}=4.39$, $w=1/(\sigma(F_o)^2+(PWT\cdot F_o)^2+QWT)-F_o$ (for $PWT=0.020$, $QWT=1.0$).[26] All calculations were performed on a VAX 785 computer. Non-hydrogen scattering factors were taken from Cromer and Waber.[27]

Atomic coordinates, bond lengths and bond angles for the two compounds are given in Table II–IV.

TABLE II

Atomic coordinates and equivalent isotropic thermal parameters for $[Et_4N]\{OWS_3(CuCN)[Ag(PPh_3)_2]\}$; $B_{eq}=4/3\Sigma_i\Sigma_jB_{ij}a_ia_j$.

Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
W	0.93544(6)	0.0287(1)	0.75218(6)	3.82(2)
Ag	1.0293(1)	0.2448(2)	0.73553(9)	3.71(3)
Cu	0.8883(2)	0.1293(4)	0.8430(2)	4.68(7)
S1	0.9073(4)	0.2334(8)	0.7626(3)	4.3(1)
S2	1.0393(4)	0.0021(6)	0.7367(4)	4.9(2)
S3	0.9238(6)	−0.0664(8)	0.8355(5)	9.5(2)
P1	1.1079(3)	0.3186(7)	0.8260(3)	3.3(1)
P2	1.0195(3)	0.3282(7)	0.6341(3)	3.4(1)
O	0.878(1)	−0.035(3)	0.689(1)	8.6(6)
N	0.816(2)	0.199(4)	0.944(2)	7.8(8)
C	0.846(1)	0.194(3)	0.915(2)	7.8(8)
C111	1.102(1)	0.229(2)	0.8928(9)	2.0(3)*
C112	1.042(2)	0.248(3)	0.915(1)	4.7(6)*
C113	1.035(2)	0.173(3)	0.986(2)	4.9(6)*
C114	1.083(2)	0.091(4)	0.992(2)	5.9(7)*
C115	1.137(2)	0.071(4)	0.968(2)	6.3(8)*
C116	1.151(2)	0.145(3)	0.920(2)	5.0(6)*
C121	1.197(1)	0.309(3)	0.819(1)	4.1(5)*
C122	1.220(1)	0.196(3)	0.803(1)	4.0(5)*
C123	1.286(2)	0.172(4)	0.792(2)	5.9(7)*
C124	1.331(2)	0.283(4)	0.799(2)	5.5(7)*
C125	1.309(2)	0.400(4)	0.818(2)	6.0(8)*
C126	1.241(1)	0.407(3)	0.831(1)	3.3(4)*
C131	1.096(1)	0.486(2)	0.8429(9)	2.5(3)*
C132	1.122(1)	0.528(4)	0.904(1)	4.4(5)*
C133	1.116(2)	0.654(3)	0.915(1)	4.7(6)*
C134	1.082(2)	0.741(5)	0.871(2)	6.9(9)*
C135	1.053(2)	0.683(5)	0.811(2)	7.3(9)*
C136	1.060(1)	0.566(2)	0.800(1)	3.4(5)*
C211	0.995(1)	0.495(2)	0.629(1)	3.1(4)*
C212	1.028(1)	0.588(3)	0.607(1)	3.5(4)*
C213	1.006(1)	0.716(3)	0.606(1)	3.8(5)*
C214	0.951(2)	0.748(5)	0.625(2)	7.2(9)*
C215	0.912(3)	0.653(6)	0.646(3)	9(1)*
C216	0.933(2)	0.523(6)	0.648(2)	8(1)*
C221	1.099(1)	0.331(2)	0.605(1)	2.9(4)*
C222	1.159(2)	0.327(4)	0.646(2)	5.3(7)*
C223	1.222(3)	0.326(5)	0.627(2)	8(1)*
C224	1.217(3)	0.322(5)	0.562(2)	8(1)*
C225	1.157(2)	0.330(4)	0.524(2)	5.7(7)*
C226	1.097(1)	0.336(3)	0.545(1)	4.4(5)*
C231	0.956(2)	0.251(4)	0.574(2)	5.2(6)*
C232	0.913(2)	0.322(3)	0.533(2)	4.9(6)*
C233	0.874(2)	0.244(4)	0.485(2)	6.5(8)*
C234	0.876(3)	0.112(6)	0.483(3)	9(1)*
C235	0.926(3)	0.052(6)	0.524(3)	9(1)*
C236	0.966(2)	0.118(4)	0.570(2)	6.1(8)*
N1	0.696(1)	0.098(3)	0.627(1)	5.1(5)*

TABLE II *Continued.*
Atomic coordinates and equivalent isotropic thermal parameters for $[Et_4N]\{OWS_3(CuCN)[Ag(PPh_3)_2]\}$; $B_{eq}=4/3\Sigma_i\Sigma_jB_{ij}a_ia_j$.

Atom	*x/a*	*y/b*	*z/c*	$B(Å^2)$
C1	0.707(3)	0.045(6)	0.558(3)	4(1)**
C1′	0.726(5)	−0.014(9)	0.616(4)	7(2)**
C2	0.758(4)	−0.019(9)	0.557(4)	13(2)*
C3	0.618(4)	0.147(8)	0.600(4)	6(2)**
C3′	0.640(9)	0.13(2)	0.568(8)	12(4)**
C4	0.573(3)	0.032(7)	0.574(3)	10(1)*
C5	0.757(3)	0.188(6)	0.635(3)	4(1)**
C5′	0.730(5)	0.217(9)	0.644(4)	7(2)**
C6	0.746(4)	0.308(8)	0.603(3)	12(2)*
C7′	0.656(5)	0.08(1)	0.678(5)	8(2)**
C7	0.701(4)	−0.007(7)	0.666(3)	6(1)**
C8	0.705(6)	0.06(1)	0.737(5)	16(3)*

*Starred atoms were refined isotropically; doubly starred atoms were disordered and multiplicity was fixed at 0.5.

TABLE III
Selected bond lengths (Å).

Atom 1	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*
W	Ag	3.027(1)	Cu	S1	2.229(4)
W	Cu	2.653(2)	Cu	S3	2.202(5)
W	S1	2.257(5)	Cu	C	2.09(3)
W	S2	2.195(4)	P1	C111	1.82(2)
W	S3	2.195(6)	P1	C121	1.83(1)
W	O	1.79(1)	P1	C131	1.83(1)
Ag	S1	2.636(4)	P2	C211	1.83(1)
Ag	S2	2.570(3)	P2	C221	1.85(1)
Ag	P1	2.455(4)	P2	C231	1.86(2)
Ag	P2	2.439(4)	N	C	0.98(3)

RESULTS AND DISCUSSION

Synthesis

Because the cyano ligands are easily displaced in their anions, complexes of thiomolybdates with Cu(I) and Ag(I) cyanides are useful starting materials for synthesis. Displacement by thiolato ligands produces thiolatocopper(I)-tetrathiomolybdate(VI)$^{6(a)}$ as shown below.

$$[(CN)CuS_2MoS_2]^{2-}+PhS^- \rightarrow [(PhS)CuS_2MoS_2]^{2-}$$

$$[(CN)CuS_2MoS_2Cu(CN)]^{2-}+2PhS^- \rightarrow [(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$$

TABLE IV

Selected bond angles (°).

Atom 1	*Atom 2*	*Atom 3*	*Angle*	*Atom 1*	*Atom 2*	*Atom 3*	*Angle*
Ag	W	Cu	96.93(5)	W	S1	Ag	76.1(2)
Ag	W	O	119.8(7)	W	S1	Cu	72.5(1)
Cu	W	O	120.5(5)	Ag	S1	Cu	122.0(2)
S1	W	S2	113.7(1)	W	S2	Ag	78.5(2)
S1	W	S3	106.1(2)	W	S3	Cu	74.2(2)
S2	W	S3	110.2(2)	Ag	P1	C111	113.6(4)
S1	W	O	107.9(6)	Ag	P1	C121	112.4(5)
S2	W	O	107.5(5)	Ag	P1	C131	113.1(4)
S3	W	O	111.4(7)	C111	P1	C121	105.7(7)
S1	Ag	S2	91.5(1)	C111	P1	C131	107.4(5)
S1	Ag	P1	106.9(1)	C121	P1	C131	103.9(6)
S2	Ag	P1	105.7(1)	Ag	P2	C211	112.5(4)
S1	Ag	P2	109.4(1)	Ag	P2	C221	115.8(4)
S2	Ag	P2	111.2(1)	Ag	P2	C231	116.6(6)
P1	Ag	P2	126.5(1)	C211	P2	C221	101.4(6)
W	Cu	C	174.9(4)	C211	P2	C231	103.6(7)
S1	Cu	S3	106.8(3)	C221	P2	C231	105.2(7)
S1	Cu	C	129.5(4)	Cu	C	N	160(2)
S3	Cu	C	123.7(5)				

Displacement by triphenylphosphine leads to triphenylphosphine-copper(I)-tetrathiomolybdate(VI) [or tungstate(VI)] complexes[9] as follows.

$$[(CN)CuS_2MS_2]^{2-} + [(PPh_3)_2Cu(NO_3)] \rightarrow [(PPh_3)_3Cu_2MS_4]$$

$$[(CN)AgS_2WS_2]^{2-} + [(PPh_3)_2Cu(NO_3)] \rightarrow [(PPh_3)_3CuAgWS_4]$$

In our procedures the cyano ligands are not displaced by triphenylphosphine.

$$[(CN)CuS_3WO]^{2-} + [(PPh_3)_2Ag(NO_3)] \rightarrow [(CN)CuS_3OWAg(PPh_3)_2]^-$$

The only difference between our procedure and the above is the reaction temperature. Therefore, at 3–5°C the cyano ligands are relatively difficult to displace, but not at room temperature. The high yield of the product means that the OWS_2CuCN moiety of the product is relatively stable in solution at 3–5°C. When the product was recrystallized at room temperature, the complex $[(PPh_3)_3CuAgWOS_3]$ was obtained.

Structure of $[(CH_3CH_2)_4N][(PPh_3)_2\{AgS_3WOCu\}(CN)]$ (I)

The structure of the anion $[(PPh_3)_2\{AgS_3WOCu\}(CN)]^-$ is shown in Figure 1. The three different metal atoms (Ag, W, Cu) and the three bridging sulphido ligands are arranged in a butterfly structure, which is very similar to the structure of the

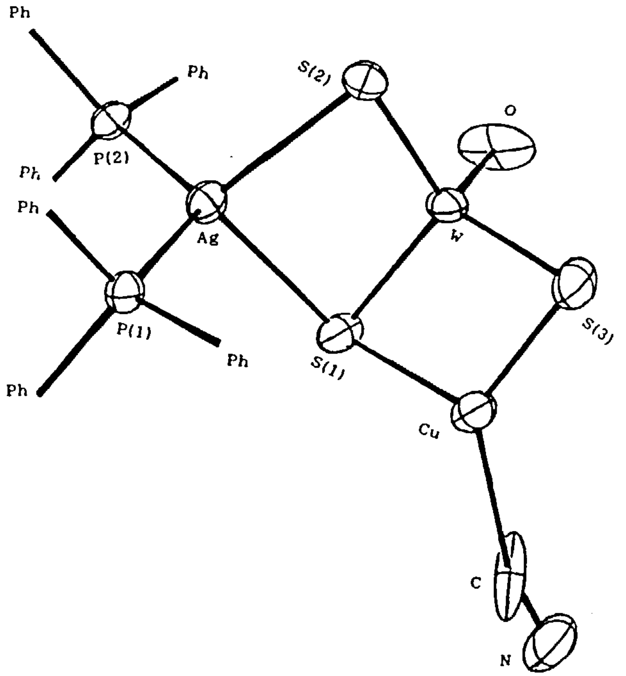

FIGURE 1 The configuration of the anion $[(Ph_3P)_2\{AgS_3WOCu\}(CN)]^-$, showing the atom labelling scheme.

bimetallic complex $[(PPh_3)\{CuMoOS_3Cu\}(PPh_3)_2]$.[20] The Ag–W–Cu angle is approximately 96.93(5)°. In the anion, the W atom has tetrahedral coordination by two μ_2-S, one μ_3-S and one terminal oxygen atom as in WOS_3^{2-}. The Cu atom is approximately trigonal planar (with one μ_3-S, one μ_2-S and one CN ligand), but the Ag atom is tetrahedrally coordinated by one μ_2-S, one μ_3-S and two PPh_3 ligands. The W-(μ_3-S) bond is 0.06 Å longer than the other two W–S bonds. The Et_4N^+ cation is disordered.

WS_2Cu and WS_2Ag groups are planar to within 0.042 and 0.051 Å, respectively. The dihedral angle is 52.1(2)°. Because the W and Ag atoms both have tetrahedral coordination geometries, the groups of atoms [P(1), P(2), Ag, W, O, S(3)] and [W, S(1), S(3), Cu, C, N] are almost planar, while the CN ligand is in the WCuAg plane to within 0.068 Å. The W–Cu bond is 2.653(2)Å, but the W–Ag and the Cu–Ag distances are too long to efficiently bond.

Another way to view the structure is that the WCuAg(μ_3-S) fragment forms a tetrahedrane framework. It has been demonstrated[21] that the EM_3 tetrahedrane framework ensures chirality for a cluster with three different metal atoms in which there are metal-metal bonds between any two metals. With respect to possible applications it is important to know the configurational stability of the optically active clusters. The butterfly-like complex $[(CH_3CH_2)_4N][(PPh_3)_2\{AgS_3WOCu\}(CN)]$ (I) can also be regarded as a derivative of this type of tetrahedrane framework cluster.

It is certain that the structure of the anion shares framework chirality. In the unit cell both enantiomers exist. Enantiomer stability after separation is not certain. The tetrahedral geometry of the OWS_3 moiety is very stable and should prevent one enantiomer inverting to the other; the two enantiomers might be able to be separated. In solution, the simplest way to racemize each enantiomer is through breaking of the Ag-(μ_3-S) bond to form another Ag-(μ_3-S) bond. Research on enantiomer separation, optical activity and applications will be of interest and will be reported in the future.

The presence of coordinated cyanide is confirmed in the IR by the presence of medium intensity, sharp absorptions at around 2120 cm^{-1}. Bands due to PPh_3 ligands are obviously distinguished. Two bands at around 515 and 505 cm^{-1} are attributed to Ag–P vibrations. The electronic spectrum of the WOS_3^{2-} anion shows[3] two intense low-energy absorptions at around 375 and 334 nm. $[OWS_3CuCN]^{2-}$ and $[OWS_3CuAg(CN)(PPh_3)_2]^-$ also exhibit two bands near these values and the spectra appear to be little influenced by the coordination of CuCN or $Ag(PPh_3)_2^+$ fragments.

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SUPPLEMENTARY MATERIAL

Lists of anisotropic thermal parameters, complete tables of bond lengths and angles and observed and calculated structure factors are available from X.T. Wu on request.

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