

Two W/Cu/S clusters: tetraethylammonium bromidodi- μ_2 -sulfido-sulfido[tris(3,5-dimethylpyrazol-1-yl)borato]copper(I)tungsten(VI) and tetraethylammonium dibromido- μ_3 -sulfido-di- μ_2 -sulfido-[tris(3,5-dimethylpyrazol-1-yl)borato]dicopper(I)tungsten(VI)

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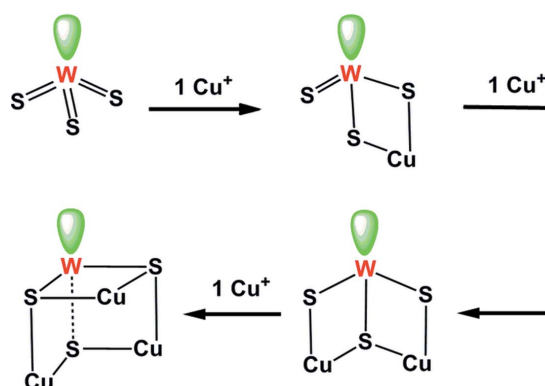
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The reaction of $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$ [Tp^* = hydrogen tris(3,5-dimethylpyrazol-1-yl)borate] with one or two equivalents of CuBr afforded the [1 + 1] and [1 + 2] addition products $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}(\mu\text{-S})_2(\text{CuBr})]$ {or $(\text{C}_8\text{H}_{20}\text{N})[\text{CuWBr}(\text{C}_{15}\text{H}_{22}\text{BN}_6)_3\text{S}_3]$, (I)} and $(\text{Et}_4\text{N})[\text{Tp}^*\text{W}(\mu_3\text{-S})(\mu\text{-S})_2(\text{CuBr})_2]$ {or $(\text{C}_8\text{H}_{20}\text{N})[\text{Cu}_2\text{WBr}_2(\text{C}_{15}\text{H}_{22}\text{BN}_6)_3\text{S}_3]$, (II)}. The anion of (I) contains a $[\text{W}(\mu\text{-S})_2\text{Cu}]$ core formed by the addition of one CuBr unit to the $[\text{Tp}^*\text{WS}_3]$ species. The anion of (II) has a butterfly-shaped $[\text{W}(\mu_3\text{-S})(\mu\text{-S})_2\text{Cu}_2]$ core formed by the addition of two CuBr units to the $[\text{Tp}^*\text{WS}_3]$ species. The $[\text{Tp}^*\text{WS}_3]$ sections of each complex exhibit approximate C_{3v} point symmetry and have closely comparable geometry. In (II), both the anion and cation lie on a crystallographic mirror plane. The structure of (I) is noncentrosymmetric and polar.

Comment

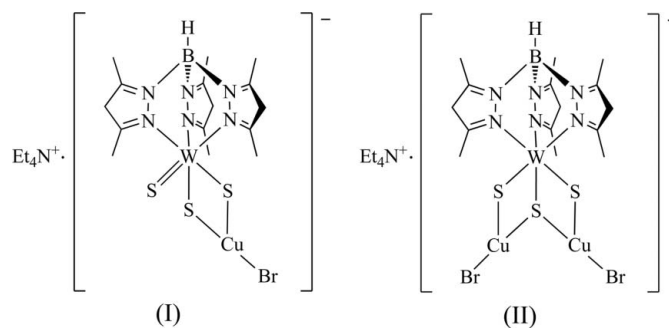
In the past decades, the chemistry of Mo(W)/Cu/S clusters derived from reactions of metal sulfide synthons such as $[\text{MO}_x\text{S}_{4-x}]^{2-}$ or $[\text{Cp}^*\text{MS}_3]^-$ ($M = \text{Mo}$ or W , $x = 0\text{--}3$, Cp^* = pentamethylcyclopentadienyl) with CuX ($X = \text{Cl}$, Br , I , NCS , CN) has been investigated extensively because of their novel structures (Chisholm *et al.*, 2002; Parkin, 2004; Zulys *et al.*, 2005) and their potential applications in biological systems (Lewinski *et al.*, 2006) and opto-electronic materials (Vahrenkamp, 1999). Among these Mo(W)/Cu/S clusters, a complete series of products obtained by the stepwise addition of CuX has not previously been realized in a system involving the same components CuX and $[\text{MS}_4]^{2-}$ or $[\text{EMS}_3]^{n-}$ ($E = \text{O}$, $n = 2$ or $E = \text{Cp}^*$, $n = 1$) in different molar ratios (Bunge *et al.*,

2007; Boomishankar *et al.*, 2006; Malik *et al.*, 1997; Kaupp *et al.*, 1991). Recently, we have investigated the preparation of Mo(W)/Cu/S clusters from the precursor $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$, where Tp^* = hydrogen tris(3,5-dimethylpyrazol-1-yl)borate (Seino *et al.*, 2001), and this compound has been found to undergo stepwise addition reactions with one to four equivalents of CuNCS to yield the products $[\text{Tp}^*\text{WS}_3(\text{CuNCS})_n]^-$ ($n = 1$ or 2), $[\text{Tp}^*\text{WS}_3(\text{CuNCS})_3\text{Br}]^{2-}$ and the polymeric $\{\text{Tp}^*\text{WS}_3(\text{CuNCS})_4\}^-$ (Wei, Li, Ren *et al.*, 2009). In a continuation of our work in this area, we treated the precursor $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$ with one to three equivalents of CuBr in a stepwise manner (Scheme 1 shows the stepwise addition of Cu^+ to the WS_3 core to construct a cubane-like unit) and



Scheme 1

obtained the [1 + 1], [1 + 2] and [1 + 3] products, $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}(\mu\text{-S})_2(\text{CuBr})]$, $(\text{Et}_4\text{N})[\text{Tp}^*\text{W}(\mu_3\text{-S})(\mu\text{-S})_2(\text{CuBr})_2]$ and $(\text{Et}_4\text{N})[\text{Tp}^*\text{W}(\mu_3\text{-S})_3(\text{CuBr})_3]$. We have reported the crystal structure of the [1 + 3] product previously (Wei, Li, Cheng *et al.*, 2009). We report herein the crystal structures of the [1 + 1] and [1 + 2] complexes, (I) and (II).



Scheme 2

The anion of complex (I) comprises a $[\text{Tp}^*\text{WS}_3]^-$ unit and one CuBr group, with a pair of $\mu\text{-S}$ atoms forming a WS_2Cu ring (Fig. 1). One terminal S atom is retained. The structure closely resembles that of the anion in the related compound $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}(\mu\text{-S})_2(\text{CuNCS})]$ (Wei, Li, Ren *et al.*, 2009). It is noteworthy that the comparable [1 + 1] addition complex is not known among the M/Cu/S clusters based on the related precursor $[\text{PPh}_3][\text{Cp}^*\text{MS}_3]$, while for the $(\text{Et}_4\text{N})[\text{OMS}_3]$

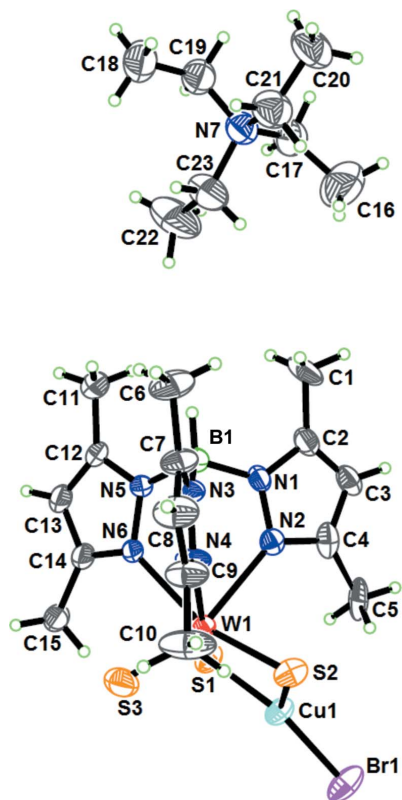


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size.

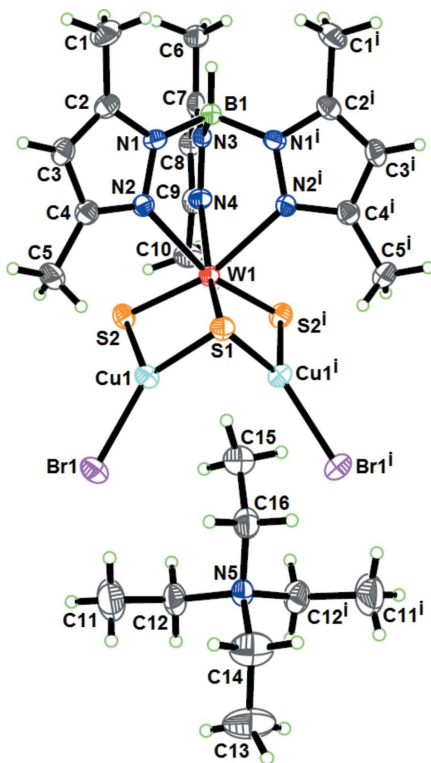


Figure 2
The molecular structure of (II), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size. Methyl H atoms on C6, C10, C13 and C15 are disordered over the mirror plane. [Symmetry code: (i) $x, -y + \frac{3}{2}, z$.]

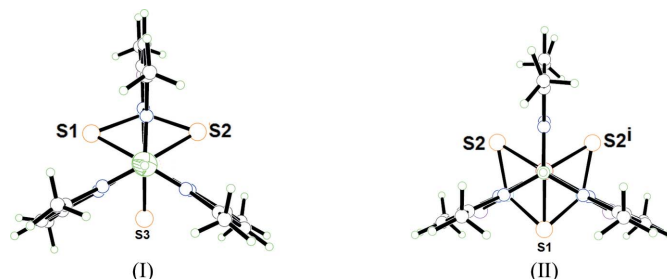


Figure 3
A view of the anions in (I) and (II) along the approximate threefold axis of the Tp* group. [Symmetry code: (i) $x, -y + \frac{3}{2}, z$.]

precursor, reactions with one equivalent of CuCl and CuCN have been reported to yield the products $[\text{Me}_4\text{N}][\text{WOS}(\mu\text{-S})_2(\text{CuCl})]$ (Shamsur Rahman *et al.*, 2000) and $(\text{Et}_4\text{N})[\text{MoOS}(\mu\text{-S})_2(\text{CuCN})]$ (Zhang *et al.*, 2008), respectively. In (I), atom Cu1 adopts a trigonal planar geometry, coordinated by one terminal Br atom and two $\mu\text{-S}$ atoms. The $\text{W1}\cdots\text{Cu1}$ distance of 2.5893 (11) Å is slightly shorter than those in other butterfly-shaped or incomplete cubane core clusters. The terminal $\text{W1}\text{—S3}$ bond length of 2.141 (3) Å is similar to that in $[\text{WS}_4\text{Cu}_2(\text{dppm})_3]$ [2.146 (4) Å; dppm = bis(diphenylphosphino)methane; Lang & Tatsumi, 1998], but slightly shorter than those in the corresponding precursor $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$ (mean 2.193 Å; Seino *et al.*, 2001) and in the cluster $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}(\mu\text{-S})_2(\text{CuNCS})]$ [2.154 (3) Å; Wei, Li, Ren *et al.*, 2009]. The mean $\text{W}\text{—}\mu\text{-S}$ (2.268 Å), $\text{Cu}\text{—}\mu\text{-S}$ (2.193 Å) and $\text{Cu}\text{—Br}$ [2.2831 (14) Å] bond lengths are slightly longer than the corresponding values in the complex $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}(\mu_3\text{-S})_3(\text{CuBr})_3]$ (Wei, Li, Cheng *et al.*, 2009).

The anion of complex (II) has a butterfly-shaped $[\text{WS}_3\text{Cu}_2]$ structure in which one $[\text{Tp}^*\text{WS}_3]$ unit and two CuBr groups are linked *via* one $\mu_3\text{-S}$ and two $\mu\text{-S}$ atoms (Fig. 2). Atoms W1, S1, B1, N3, N4 and C6–C10 lie on a crystallographic mirror plane. Similar butterfly-shaped $[\text{WS}_3\text{Cu}_2]$ cores have been observed in $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3(\text{CuNCS})_2]$ (Wei, Li, Ren *et al.*, 2009), $(\text{PPh}_4)[(\text{Cp}^*\text{WS}_3(\text{CuCN})_2)]$ (Lang *et al.*, 2004) and $[\text{MOS}_3\text{M}'_2(\text{PPh}_3)_3]$ ($M = \text{W}, \text{Mo}$; $M' = \text{Cu}, \text{Ag}$) (Müller *et al.*, 1983). Each Cu atom in (II) adopts a trigonal planar geometry, coordinated by one $\mu\text{-S}$ atom, one $\mu_3\text{-S}$ atom and one terminal Br atom. The $\text{W}\cdots\text{Cu}$ distance of 2.6239 (10) Å is longer than that in complex (I), but similar to those found in other complexes containing three-coordinated Cu, such as $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}(\mu_3\text{-S})_3(\text{CuBr})_3]$ [2.6404 (2) Å; Wei, Li, Cheng *et al.*, 2009] and $(\text{PPh}_4)[\text{Cp}^*\text{WS}_3(\text{CuCN})_2]$ [2.666 (3) Å; Lang *et al.*, 2004]. Because of the coordination of the S atoms to the Cu atoms, the $\text{W1}\text{—S1}$ bond length of 2.331 (2) Å is longer than the $\text{W1}\text{—S2}$ bond length of 2.2293 (18) Å, and both bonds are elongated relative to the mean $\text{W}\text{—S}$ bond length (2.193 Å) in the precursor $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$ (Seino *et al.*, 2001).

Fig. 3 illustrates how the S and Cu^{I} centres of (I) and (II) build up sequentially towards the corners of a cubane-like unit. Firstly, one Cu^{I} centre is added to the Tp^*WS_3 unit to construct the $[\text{Tp}^*\text{WS}(\mu\text{-S})_2\text{Cu}]$ core with one terminal S atom remaining. Secondly, the two Cu^{I} centres in (II) form the

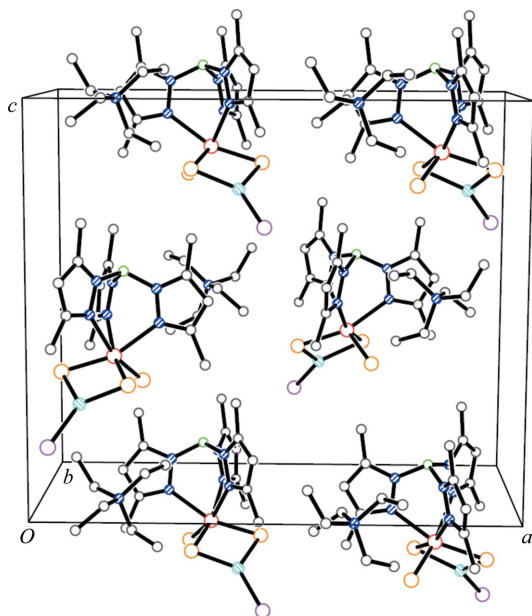


Figure 4

A packing diagram of (I), viewed along the *b* axis, showing the noncentrosymmetric and polar arrangement. H atoms have been omitted.

butterfly core $[\text{Tp}^*\text{W}(\mu\text{-S})_2(\mu_3\text{-S})\text{Cu}_2]$. A third Cu^1 centre can then be added to the butterfly core of (II) to produce an incomplete cubane-like unit, $[\text{Tp}^*\text{W}(\mu_3\text{-S})_3\text{Cu}_3]$, as in the previously published structure $(\text{Et}_4\text{N})[\text{Tp}^*\text{W}(\mu_3\text{-S})_3(\text{CuBr})_3]$ (Wei, Li, Cheng *et al.*, 2009). Throughout this sequence, the geometry of the $[\text{Tp}^*\text{WS}_3]$ unit remains essentially unchanged: the r.m.s. deviations for overlay of the 26 non-H atoms in the core onto the precursor $[\text{Tp}^*\text{WS}_3]$ are 0.14, 0.10 and 0.30 Å for (I), (II) and $(\text{Et}_4\text{N})[\text{Tp}^*\text{W}(\mu_3\text{-S})_3(\text{CuBr})_3]$, respectively. The $[\text{Tp}^*\text{WS}_3]$ unit exhibits approximate C_{3v} point symmetry and one of the mirror planes is retained as a crystallographic symmetry element in (II).

Packing diagrams are shown for (I) and (II) in Figs. 4 and 5, respectively. The structures contain comparable stacks of alternating complexes and Et_4N^+ cations running along the *b* axes. In (I), these stacks are arranged so that the Cu–Br bonds point towards the same direction along the *c* axis, forming a noncentrosymmetric and polar structure. In (II), the stacks are arranged in a centrosymmetric manner.

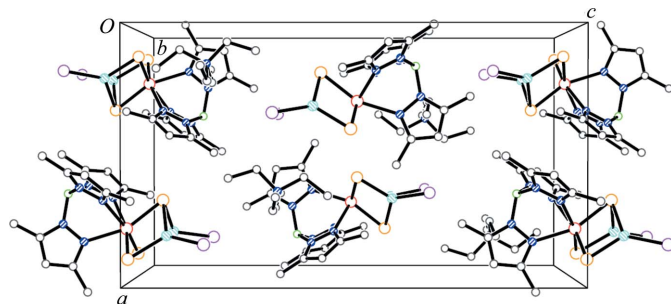


Figure 5

A packing diagram of (II), viewed along the *b* axis, showing the centrosymmetric arrangement. H atoms have been omitted.

Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk-line techniques. The precursor $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$ was prepared as reported previously (Seino *et al.*, 2001). For these reactions, CHCl_3 is a better solvent than MeCN because CuBr is poorly soluble in CHCl_3 and it can facilitate the stepwise introduction of CuBr into $[\text{Tp}^*\text{WS}_3]^-$. Compound (I) is air sensitive and easily oxidized in solution to form $(\text{Et}_4\text{N})[\text{Tp}^*\text{WO}(\mu\text{-S})_2(\text{CuBr})]$. Complex (II) is relatively air and moisture stable in the solid state.

For the synthesis of (I), CuBr (14.4 mg, 0.1 mmol) was added to a solution of $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$ (75 mg, 0.1 mmol) in CHCl_3 (15 ml). After being stirred for half an hour, the resulting red solution was filtered and Et_2O (30 ml) was carefully layered onto the surface of the filtrate. After 4 d, red prisms of (I) were collected by filtration, washed with Et_2O and dried *in vacuo* [yield 72.3 mg, 80% based on $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$]. Analysis calculated: C 32.46, H 4.98, N 11.52%; found C 32.32, H 4.55, N 11.95%. IR (KBr disc, cm^{-1}): 2978 (*m*), 2920 (*m*), 2554 (*w*), 1628 (*w*), 1546 (*s*), 1440 (*s*), 1435 (*s*), 1418 (*s*), 1035 (*m*), 860 (*w*), 806 (*w*), 691 (*w*), 651 (*w*), 459 (*m*), 416 (*w*). UV–visible {MeCN, λ_{max} [nm ($\epsilon M^{-1} \text{cm}^{-1}$)]}: 333 (14300), 445 (6400), 524 (3000). ^1H NMR (400 MHz, CDCl_3): δ 1.36–1.40 (*t*, 12H, CH_2CH_3), 2.37 (*s*, 9H, CH_3 in Tp^*), 2.95 (*s*, 9H, CH_3 in Tp^*), 3.33–3.39 (*q*, 8H, CH_2CH_3), 5.94 (*s*, 3H, CH in Tp^*), the B–H proton was not identified.

For the synthesis of (II), CuBr (28.8 mg, 0.2 mmol) was added to a solution of $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$ (75 mg, 0.1 mmol) in CHCl_3 (15 ml). A procedure identical to that used for (I) afforded dark red blocks of (II) [yield 93 mg, 85% based on $(\text{Et}_4\text{N})[\text{Tp}^*\text{WS}_3]$]. Analysis calculated: C 27.78, H 4.26, N 9.86%; found: C 27.32; H 4.55; N 9.95%. IR (KBr disc, cm^{-1}): 2979 (*m*), 2921 (*m*), 2554 (*w*), 1628 (*w*), 1546 (*s*), 1440 (*s*), 1435 (*s*), 1418 (*s*), 1035 (*m*), 860 (*w*), 806 (*w*), 693 (*w*), 651 (*w*), 469 (*w*), 420 (*w*). UV–visible {MeCN, λ_{max} [nm ($\epsilon M^{-1} \text{cm}^{-1}$)]}: 323 (16300), 420 (8890), 544 (5800). ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.36–1.40 (*t*, 12H, CH_2CH_3), 2.37 (*s*, 9H, CH_3 in Tp^*), 2.96 (*s*, 9H, CH_3 in Tp^*), 3.31–3.38 (*q*, 8H, CH_2CH_3), 5.92 (*s*, 3H, CH in Tp^*), the B–H proton was not identified.

Compound (I)

Crystal data

$(\text{C}_8\text{H}_{20}\text{N})[\text{CuWBr}(\text{C}_{15}\text{H}_{22}\text{BN}_6)\text{S}_3]$	$V = 3196.6 (11) \text{ \AA}^3$
$M_r = 850.95$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 19.058 (4) \text{ \AA}$	$\mu = 5.73 \text{ mm}^{-1}$
$b = 10.276 (2) \text{ \AA}$	$T = 293 \text{ K}$
$c = 16.323 (3) \text{ \AA}$	$0.35 \times 0.30 \times 0.25 \text{ mm}$

Data collection

Rigaku Mercury CCD diffractometer	29584 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	5857 independent reflections
$T_{\text{min}} = 0.147$, $T_{\text{max}} = 0.239$	5342 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{\text{max}} = 1.05 \text{ e \AA}^{-3}$
$wR(F^2) = 0.084$	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
$S = 1.10$	Absolute structure: Flack (1983),
5710 reflections	2678 Friedel pairs
344 parameters	Flack parameter: 0.004 (10)
84 restraints	
H-atom parameters constrained	

Compound (II)

Crystal data

$(C_8H_{20}N)[Cu_2WBr_2(C_{15}H_{22}BN_6)_3S_3]$	$V = 3401.7 (12) \text{ \AA}^3$
$M_r = 994.40$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 12.808 (3) \text{ \AA}$	$\mu = 7.17 \text{ mm}^{-1}$
$b = 11.768 (2) \text{ \AA}$	$T = 293 \text{ K}$
$c = 22.569 (5) \text{ \AA}$	$0.40 \times 0.30 \times 0.17 \text{ mm}$

Data collection

Rigaku Mercury CCD diffractometer	32255 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	3282 independent reflections
$T_{\min} = 0.087, T_{\max} = 0.295$	2999 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.120$	$\Delta\rho_{\max} = 1.48 \text{ e \AA}^{-3}$
$S = 1.09$	$\Delta\rho_{\min} = -1.15 \text{ e \AA}^{-3}$
3276 reflections	
206 parameters	

H atoms were placed geometrically and constrained to ride on their parent atoms, with B—H = 0.98 Å and C—H = 0.96 (methyl), 0.97 (methylene) or 0.93 Å (aromatic), and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms or $1.2U_{\text{eq}}(\text{C})$ otherwise. In (I), extensive rigid-bond and similarity restraints were applied to the displacement parameters of atoms C4, C5, C9, C10, N7 and C16–C23. In (II), the methyl H atoms on C6 and C10 (in the pyrazole ring) and on C13 and C15 (in the Et_4N^+ cation) are disordered over the mirror plane.

For both compounds, data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3020). Services for accessing these data are described at the back of the journal.

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