

Synthesis and X-Ray Crystal Structure of Acetonitriletetrakis(2,4,6-tri-isopropylthiophenolato)molybdenum(IV)*

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[MoCl₃(NCCH₃)₃] reacts with an excess of 2,4,6-tri-isopropylthiophenolate in acetonitrile to give [Mo(SC₆H₂Prⁱ₃-2,4,6)₄(NCCH₃)₃] where molybdenum has been oxidized. An X-ray crystal structure determination revealed a trigonal-bipyramidal geometry about molybdenum with a CH₃CN group occupying an apical site.

There are presently no known instances of metal-thiolate cores co-ordinating or even interacting with dinitrogen. We have been investigating potential binding sites for dinitrogen using sterically hindered thiophenolate co-ligands. Recent work has shown that [Mo(tipt)₄] (tipt = SC₆H₂Prⁱ₃-2,4,6) can be synthesised from MoCl₅ and SiMe₃(tipt)¹ or by reaction of [MoCl₄(thf)₂] (thf = tetrahydrofuran) with Na(tipt).² The X-ray crystal structure of [Mo(tipt)₄] revealed an approximately tetrahedral geometry about molybdenum.¹ No interaction with dinitrogen was detectable, which led us to investigate the reactivity of [MoCl₃(NCCH₃)₃] with Htipt in the hope of synthesising [Mo(tipt)₄]⁻ where the added negative charge might enhance any possible dinitrogen interaction. Recent electrochemical studies² have shown that [Mo(tipt)₄] undergoes two quasi-reversible reduction couples, suggesting that anionic thiolate species may exist at least transiently.

Results and Discussion

Reaction of [MoCl₃(NCCH₃)₃] in dry acetonitrile under reflux with an excess of 2,4,6-tri-isopropylthiophenolate yielded a diamagnetic dark brown crystalline material analysing as [Mo(tipt)₄(NCCH₃)] (1). The source of oxidation in the reaction is not clear, but adventitious traces of oxygen may be responsible. The expected [Mo(tipt)₄(NCCH₃)]⁻ product is likely to be very readily oxidised. The reaction mixture turns blue on standing even under N₂, due to the formation of [MoO(tipt)₄]⁻ which remains in solution.

Complex (1) is air sensitive and rapidly decomposes in solution in air or in oxygen-donor solvents to give molybdenum oxo-complexes. Nitrogen analysis was often inconsistent, due to the presence of variable amounts of acetonitrile of crystallisation which is removed by drying *in vacuo* at 60 °C. The 80-MHz ¹H n.m.r. spectrum of (1) displays a complex series of overlapping resonances in the methyl region making assignment difficult and suggesting that a high degree of asymmetry exists in the molecule. This is confirmed by the complexity of the methine region (associated with isopropyl groups) where at least two overlapping heptets are observed. A pseudo-triplet centred at 6.98 p.p.m. indicates that the aromatic protons on the tipt ligands are not equivalent. In free Htipt a singlet is observed for the aromatic protons. The presence of a co-ordinated acetonitrile was confirmed by a weak i.r. absorption band at 2 270 cm⁻¹. There is also a weak band at 2 285 cm⁻¹ indicating the presence of unco-ordinated acetonitrile.

The reaction of complex (1) with carbon monoxide at 1 atm

(ca. 10⁵ Pa) was investigated and gave a mixture of unstable CO-containing compounds [$\nu(\text{CO})$ 1 820, 1 900, and 1 980 cm⁻¹]. No pure carbonyl complexes could be isolated from the mixture, consistent with the observations reported in ref. 1. No interaction with dinitrogen was observed in hexane solutions at 1 or 7 atm of dinitrogen pressure. Cyclic voltammetry was utilised to monitor the reaction at elevated dinitrogen pressures.

Recent work¹ has described the synthesis of a paramagnetic complex formulated as [Mo(tipt)₄(NCCH₃)] made by reaction of [Mo(tipt)₄] with CH₃CN. Since ¹H n.m.r. spectra clearly indicated that complex (1) of the same empirical formula is diamagnetic we undertook an X-ray crystal structure of (1) to resolve this apparent anomaly.

X-Ray Analysis Results.—In the crystal, there are two independent, virtually identical molecules of [Mo(tipt)₄(NCCH₃)] denoted A and B with atoms designated Mo(1a), S(1a) *etc.* and Mo(1b), S(1b) *etc.* Atomic parameters are listed in Table 1; selected bond dimensions are in Table 2. Figures 1 and 2 are ORTEP views of one of the molecules.

Each molecule has trigonal-bipyramidal co-ordination about Mo with the CH₃CN ligand in an axial site. Two of the equatorial thiolate ligands are pointed in the same direction as the acetonitrile (*endo*); the third is turned in the opposite direction (*exo*). This orientation of thiolate ligands has been observed before and it has been reasoned that steric compressions determined this conformation.³ The (CH₃)N—Mo—S—C torsion angles of the *endo* ligands lie in the range 2.2–6.4° and those in the *exo* ligands are 175.2 and 176.5°, *i.e.* almost 'straight up and down' (Figure 2). The similarities between the two molecules extend to the orientations of most of the isopropyl groups, in spite of the fact that the two have different orientations and environments in the cell.

In the Mo co-ordination sphere the Mo—S(axial) bond lengths are less than those found in similar trigonal-bipyramidal complexes (Table 3). Direct structural comparison of complex (1) with [Ru(tipt)₄(NCCH₃)] reveals similar M—S(axial) bond lengths but the Mo—S(equatorial) bonds are significantly longer than those of the Ru complex. However, in the absence of structural data for other complexes of the same stoichiometry, the reasons for this are not yet clear.

There are two sites for the solvent CH₃CN molecules in the crystal lattice. Each is in a cleft in the Mo complex (Figure 1), lying roughly in the same plane as the CH₃CN ligand and S(2), and between two 'endo' tipt ligands, occupying the space that would be taken by a third 'endo' ligand. The site of the solvent molecule of N(9), close to molecule A, appears fully occupied; that of N(8), close to molecule B, has been refined with an occupancy factor of 0.5, but we are unable by limitations in our refinement programs to resolve these molecules completely. The

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

molecule of N(8) appears to have fewer intermolecular contacts than N(9) and may in fact have more volume to occupy in a more disordered way; *i.e.* the occupancy factor may be an underestimate. The complexes and solvent molecules are separated by normal van der Waals distances.

Experimental

Synthesis.—All reactions were carried out under dinitrogen using dry solvents and conventional Schlenk-line techniques. Microanalyses were obtained from the University of Sussex, School of Chemistry and Molecular Sciences. I.r. spectra were recorded on a Perkin-Elmer 1330 spectrophotometer and ¹H n.m.r. spectra on a Bruker 80 MHz multinuclear instrument. [MoCl₃(NCCH₃)₃]⁴ and 2,4,6-tri-isopropylthiophenol³ were synthesised according to our modified literature method.

Synthesis of Acetonitriletetrakis(2,4,6-tri-isopropylthiophenolato)molybdenum(IV), [Mo(tipt)₄(NCCH₃)] (I).—To a suspension of [MoCl₃(NCCH₃)₃] (0.2 g, 0.61 mmol) in acetonitrile (50 cm³) was added 2,4,6-tri-isopropylthiophenol (0.85 g, 3.6 mmol) and an equivalent amount of triethylamine (0.3 g, 3.6 mmol, *D* = 0.726 g cm⁻³). The resulting dark yellow solution was stirred at room temperature for *ca.* 2 h. Filtration followed by evaporation of the solvent to half volume gave traces of crystalline product. The suspension was then left for a further 12 h by which time a significant amount of crystalline product had precipitated from solution (yield 0.43 g, 51% based on Mo starting material). This was dried *in vacuo* at 60 °C prior to analysis (Found: C, 68.8; H, 8.6; N, 1.3. C₆₂H₉₅MoNS₄ requires C, 69.0; H, 8.9; N, 1.3%; δ_H(CDCl₃), 0.8–1.5 (21 H, m, CH₃), 2.7–3.8 (3 H, m, CH), and 6.98 (2 H, t, C₆H₂). I.r. (Nujol mull): ν(C≡N) at 2 270 and 2 285 w cm⁻¹.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Mo(1a)	5 909.9(4)	2 562.6(2)	8 728.4(2)	Mo(1b)	6 063.3(4)	2 276.2(2)	3 604.3(2)
S(1a)	5 832(1)	2 537.5(8)	9 682.6(7)	S(1b)	6 157(2)	3 097.8(8)	3 009.1(9)
C(11a)	4 581(5)	2 460(3)	9 779(3)	C(11b)	7 448(5)	3 036(3)	2 898(3)
C(12a)	3 837(5)	2 997(3)	9 827(3)	C(12b)	8 155(7)	3 301(4)	3 279(3)
C(13a)	2 901(6)	2 922(4)	9 922(3)	C(13b)	9 084(7)	3 343(4)	3 130(3)
C(14a)	2 691(5)	2 344(4)	9 959(3)	C(14b)	9 316(6)	3 114(4)	2 630(3)
C(15a)	3 443(5)	1 832(3)	9 903(3)	C(15b)	8 631(6)	2 822(4)	2 297(3)
C(16a)	4 404(5)	1 860(3)	9 819(3)	C(16b)	7 681(5)	2 777(3)	2 412(3)
C(121a)	3 996(8)	3 660(4)	9 787(5)	C(121b)	7 965(9)	3 559(5)	3 827(4)
C(122a)	3 158(16)	4 102(6)	9 357(6)	C(122b)	8 997(12)	3 400(9)	4 320(5)
C(123a)	4 029(11)	3 942(5)	10 372(6)	C(123b)	7 443(13)	4 250(6)	3 723(6)
C(141a)	1 621(6)	2 297(5)	10 041(5)	C(141b)	10 316(7)	3 179(6)	2 468(5)
C(142a)	1 662(8)	1 722(7)	10 388(5)	C(142b)	10 089(11)	3 586(11)	1 978(7)
C(143a)	745(7)	2 579(8)	9 536(5)	C(143b)	11 174(10)	3 164(13)	2 906(7)
C(161a)	5 216(5)	1 261(3)	9 791(3)	C(161b)	6 995(5)	2 456(3)	2 014(3)
C(162a)	4 773(7)	781(4)	9 438(4)	C(162b)	7 586(8)	1 779(5)	1 940(6)
C(163a)	5 821(7)	944(4)	10 417(4)	C(163b)	6 464(9)	2 867(6)	1 443(5)
S(2a)	6 286(1)	1 586.4(7)	8 371.7(7)	S(2b)	6 035(1)	1 350.8(8)	3 168.9(7)
C(21a)	7 655(4)	1 288(3)	8 391(3)	C(21b)	4 749(5)	1 230(3)	2 920(3)
C(22a)	8 395(5)	1 014(3)	8 909(3)	C(22b)	4 049(5)	1 565(3)	2 412(3)
C(23a)	9 464(5)	782(3)	8 897(3)	C(23b)	3 066(5)	1 439(3)	2 234(3)
C(24a)	9 753(5)	809(3)	8 390(3)	C(24b)	2 777(6)	990(4)	2 537(3)
C(25a)	9 006(5)	1 055(3)	7 896(3)	C(25b)	3 487(6)	672(3)	3 023(3)
C(26a)	7 944(5)	1 307(3)	7 873(3)	C(26b)	4 476(5)	779(3)	3 236(3)
C(221a)	8 102(5)	929(3)	9 475(3)	C(221b)	4 334(5)	2 032(3)	2 036(3)
C(222a)	7 956(6)	276(4)	9 563(4)	C(222b)	4 675(6)	1 700(4)	1 534(3)
C(223a)	8 905(7)	1 089(4)	9 994(3)	C(223b)	3 426(7)	2 646(4)	1 806(4)
C(241a)	10 950(6)	558(4)	8 410(4)	C(241b)	1 703(7)	862(6)	2 305(4)
C(242a)	11 621(8)	908(7)	8 729(7)	C(242b)	962(11)	1 136(11)	2 569(10)
C(243a)	11 278(7)	-146(4)	8 465(6)	C(243b)	1 588(10)	588(7)	1 762(5)
C(261a)	7 144(5)	1 573(3)	7 294(3)	C(261b)	5 257(6)	379(4)	3 767(3)
C(262a)	6 570(7)	1 067(4)	7 051(3)	C(262b)	5 924(8)	-226(5)	3 609(4)
C(263a)	7 636(7)	1 813(4)	6 830(3)	C(263b)	4 691(9)	176(5)	4 204(4)
S(3a)	5 523(1)	3 463.3(8)	8 101.0(8)	S(3b)	6 118(1)	2 331.6(9)	4 568.2(7)
C(31a)	4 157(5)	3 759(3)	7 719(3)	C(31b)	7 419(5)	2 155(3)	5 046(3)
C(32a)	3 668(5)	3 414(3)	7 310(3)	C(32b)	8 062(5)	1 563(4)	5 158(3)
C(33a)	2 562(5)	3 668(3)	7 049(3)	C(33b)	9 098(6)	1 462(4)	5 536(3)
C(34a)	1 997(5)	4 222(4)	7 175(4)	C(34b)	9 449(6)	1 927(4)	5 787(3)
C(35a)	2 528(6)	4 570(3)	7 538(4)	C(35b)	8 773(6)	2 512(4)	5 694(3)
C(36a)	3 622(5)	4 351(3)	7 826(3)	C(36b)	7 736(5)	2 660(3)	5 330(3)
C(321a)	4 248(5)	2 827(3)	7 110(3)	C(321b)	7 699(6)	979(4)	4 938(3)
C(322a)	3 617(7)	2 357(5)	6 883(4)	C(322b)	8 563(8)	434(4)	4 812(5)
C(323a)	4 797(7)	2 992(5)	6 652(4)	C(323b)	7 156(8)	733(5)	5 371(5)
C(341a)	819(6)	4 489(6)	6 936(5)	C(341b)	10 544(7)	1 836(7)	6 153(4)
C(342a)	273(8)	4 363(8)	7 394(7)	C(342b)	11 348(9)	1 822(10)	5 835(8)
C(343a)	410(10)	4 243(14)	6 433(8)	C(343b)	10 651(8)	1 908(9)	6 741(5)
C(361a)	4 173(7)	4 775(4)	8 195(4)	C(361b)	6 955(6)	3 318(4)	5 254(3)
C(362a)	4 926(8)	5 041(4)	7 896(5)	C(362b)	6 083(7)	3 303(4)	5 572(4)
C(363a)	3 436(9)	5 352(4)	8 378(5)	C(363b)	7 487(9)	3 865(5)	5 477(4)

Table 1 (continued)

Atom	x	y	z	Atom	x	y	z
S(4a)	7 688(1)	2 603.2(7)	8 988.8(7)	S(4b)	4 211(1)	2 614.0(8)	3 424.7(7)
C(41a)	7 904(4)	3 372(3)	8 911(3)	C(41b)	3 709(5)	3 065(3)	3 950(3)
C(42a)	7 919(5)	3 753(3)	9 367(3)	C(42b)	3 551(6)	3 708(3)	3 914(3)
C(43a)	8 247(6)	4 304(3)	9 325(3)	C(43b)	3 061(7)	4 044(4)	4 306(4)
C(44a)	8 507(6)	4 493(3)	8 829(4)	C(44b)	2 722(7)	3 751(4)	4 700(4)
C(45a)	8 457(5)	4 114(3)	8 389(3)	C(45b)	2 902(6)	3 102(4)	4 734(3)
C(46a)	8 153(5)	3 555(3)	8 415(3)	C(46b)	3 392(5)	2 732(3)	4 372(3)
C(421a)	7 641(6)	3 578(4)	9 905(3)	C(421b)	3 884(7)	4 084(4)	3 482(4)
C(422a)	6 749(11)	4 120(5)	10 024(6)	C(422b)	4 492(11)	4 540(6)	3 776(6)
C(423a)	8 635(10)	3 349(8)	10 434(5)	C(423b)	2 946(9)	4 431(6)	2 973(6)
C(441a)	8 884(8)	5 104(4)	8 800(5)	C(441b)	2 189(10)	4 125(7)	5 124(7)
C(442a)	8 134(13)	5 679(6)	8 855(9)	C(442b)	2 913(17)	4 377(7)	5 555(7)
C(443a)	10 087(9)	4 945(6)	9 076(6)	C(443b)	1 139(14)	4 349(13)	4 903(8)
C(461a)	8 176(5)	3 155(3)	7 912(3)	C(461b)	3 547(6)	2 039(3)	4 434(3)
C(462a)	7 684(7)	3 561(4)	7 316(3)	C(462b)	3 954(8)	1 748(5)	5 073(4)
C(463a)	9 315(6)	2 752(4)	7 975(4)	C(463b)	2 504(7)	1 870(5)	4 139(5)
N(5a)	4 295(3)	2 519(2)	8 485(2)	N(5b)	7 752(4)	1 926(3)	3 779(2)
C(51a)	3 441(5)	2 522(3)	8 394(3)	C(51b)	8 632(6)	1 796(4)	3 847(3)
C(52a)	2 292(6)	2 517(5)	8 262(4)	C(52b)	9 835(6)	1 626(6)	3 954(6)
Acetonitrile solvent molecules							
N(9)*	3 413(9)	927(7)	7 771(5)	N(8)*	9 859(17)	156(10)	3 425(10)
C(91)*	4 193(11)	525(8)	7 913(5)	C(81)*	9 051(16)	127(10)	3 261(9)
C(92)*	5 269(9)	89(5)	8 077(5)	C(82)*	8 198(15)	73(9)	2 993(8)

* These atoms have site occupancy factor of 0.5, and were refined isotropically (with U_{iso}).

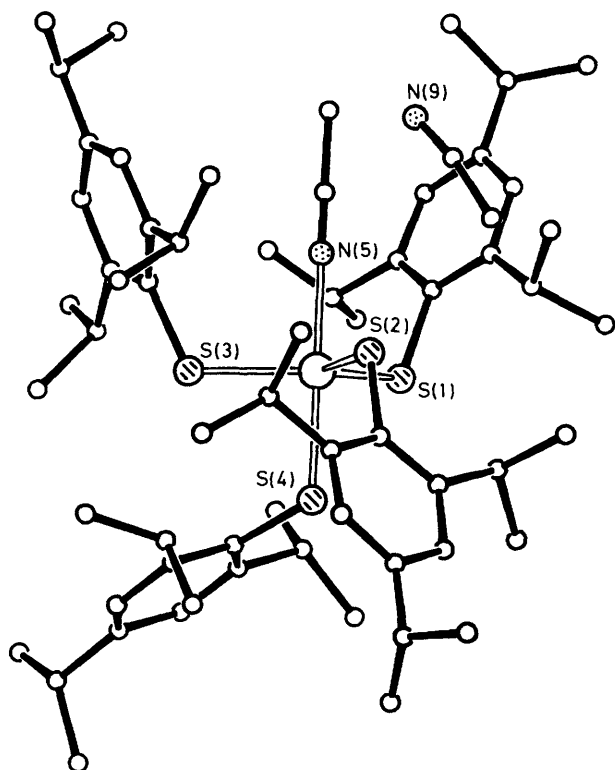


Figure 1. View of molecule A of $[\text{Mo}(\text{tipt})_4(\text{NCCH}_3)]$, whose atoms when fully labelled are Mo(1a), S(1a), S(2a) etc. A neighbouring solvent CH_3CN molecule is also shown, with its N-atom labelled N(9)

Synthesis of Tris(acetonitrile)trichloromolybdenum(III), $[\text{MoCl}_3(\text{NCCH}_3)_3]$.—Tin powder (0.65 g, 0.45 mmol) was added to a suspension of $[\text{MoCl}_4(\text{NCCH}_3)_2]$ (7.1 g, 2.2 mmol) in acetonitrile (50 cm^3). The mixture was stirred for ca. 5 h by

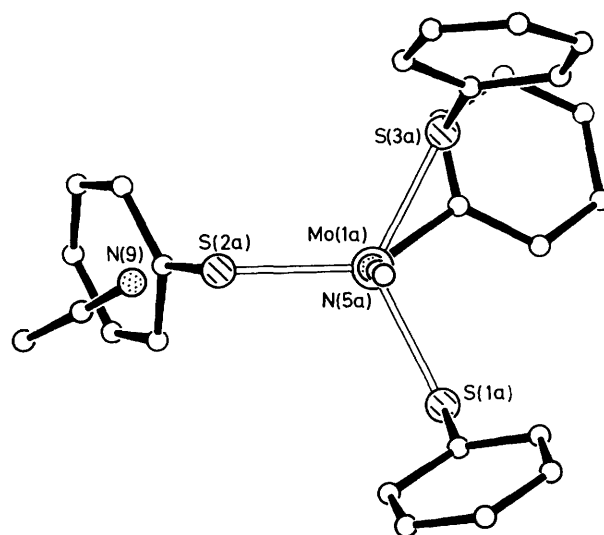


Figure 2. Molecule A and the neighbouring solvent CH_3CN molecule viewed down $\text{N}(5a) \cdots \text{S}(4a)$; the S(4a) atom is masked by the CH_3CN ligand and Mo(1a). The isopropyl substituent groups have been omitted for clarity

which time a pale yellow powder had precipitated which was collected and dried under *vacuo* (0.1 Torr, ca. 13 Pa) (yield 6.5 g, 90%) (Found: C, 22.5; H, 2.6; N, 12.6. $\text{C}_6\text{H}_9\text{Cl}_3\text{MoN}_3$ requires C, 22.1; H, 2.8; N, 12.9%).

Crystal Structure Analysis of $[\text{Mo}(\text{tipt})_4(\text{NCCH}_3)] \cdot 0.75\text{-NCCH}_3$.—Crystal data. $[\text{Mo}(\text{tipt})_4(\text{NCCH}_3)] \cdot 0.75\text{NCCH}_3$, $\text{C}_{62}\text{H}_{95}\text{MoNS}_4 \cdot 0.75\text{C}_2\text{H}_3\text{N}$, $M = 1109.4$, triclinic, $a = 13.551(3)$, $b = 21.928(3)$, $c = 24.055(3)$ Å, $\alpha = 88.04(1)$, $\beta = 104.41(2)$, $\gamma = 75.69(2)^\circ$, $U = 6673.3$ Å³, space group $P1$ (no.2), $Z = 4$, $D_c = 1.104$ g cm^{-3} , $F(000) = 2386$, $\mu(\text{Mo-K}_\alpha) = 3.5$ cm^{-1} , $\lambda(\text{Mo-K}_\alpha) = 0.71069$ Å.

Table 2. Selected bond lengths (Å) and angles (°) for [Mo(SC₆H₂-Prⁱ₃-2,4,6)₄(NCCH₃)] (molecule A)

Mo(1)-S(1)	2.323(2)	Mo(1)-S(2)	2.320(2)
Mo(1)-S(3)	2.312(2)	Mo(1)-S(4)	2.359(2)
Mo(1)-N(5)	2.148(5)	N(5)-C(51)	1.121(8)
Mo(1)-N(5)-C(51)	174.6(5)	Mo(1)-S(4)-C(31)	114.8(2)
Mo(1)-S(1)-C(11)	113.9(2)	Mo(1)-S(4)-C(31)	115.9(2)
Mo(1)-S(2)-C(21)	113.3(2)		

Table 3. Metal-sulphur distances (Å) in trigonal-bipyramidal thiolate complexes

Complex	M-S(eq) ^a	M-S(ax) ^b	Ref.
[Mo(tipt) ₄ (MeCN)]	2.316	2.358	This work
[Mo(SPh) ₄ (NO)] ⁻	2.327	2.534(2)	c
[Re(SC ₆ H ₃ Pr ⁱ ₂ -2,6) ₄ (NO)]	2.275	2.413(1)	3
[Ru(tipt) ₄ (MeCN)]	2.209	2.372(1)	d

^a Mean metal-sulphur equatorial bond length. ^b Metal-sulphur axial bond length. ^c P. T. Bishop, J. R. Dilworth, J. Hutchinson, and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1986, 967. ^d S. A. Koch and M. Millar, *J. Am. Chem. Soc.*, 1983, **105**, 3362.

The crystals are large, very dark brown plates, and unstable in air. The sample chosen for X-ray analysis was 1.0 × 0.9 × 0.25 mm and sealed in a capillary tube. After photographic examination, accurate cell dimensions (from refinement from the settings of 25 reflections with $\theta = 10\text{--}12^\circ$) and diffraction intensities were measured on an Enraf-Nonius CAD4 diffractometer with monochromated radiation. 12 411 Unique reflections ($\theta_{\text{max.}} = 25^\circ$) were measured; of these, 10 410 had $I > 2\sigma(I)$ and were used in the X-ray analysis. During processing, corrections were made for Lorentz-polarisation effects, slight deterioration of the crystal, absorption (using a semi-empirical correction), and negative intensities (by Bayesian statistical methods).

The structure was determined by direct methods; the cores of two independent molecules were evident from E-maps produced from a combination of TANG and EEES routines in

the SHELX program.⁵ Difference maps based on these fragments showed the remaining atoms in the two complex molecules. A solvent CH₃CN molecule was also located at this stage; a second solvent molecule was identified in later difference maps and was estimated to have a site occupancy factor of 0.5. There were 142 non-hydrogen atoms (all but three allowed anisotropic thermal parameters) in the refinement process which was by block-diagonal least-squares methods (BLOKLS).⁶ No methyl group H atoms were included, but H atoms on the phenyl rings and the tertiary H atoms in the isopropyl groups were included in idealised positions and set to ride on their bonded C atoms. At the conclusion of refinement, $R = 0.061$, $R' = 0.068$ for 10 404 reflections (six low θ -angle reflections were omitted with suspected extinction effects), weighted $w = (\sigma^2_F + 0.002 F_o^2)^{-1}$.

Scattering factors (for neutral atoms) were taken from ref. 7. All calculations were performed on the A.F.R.C.'s VAX 11/750 computer at Glasshouse Crops Research Institute, Littlehampton, using the programs referred to above (SHELX and BLOKLS) and in Table 4 of ref. 8.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

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