# Functionalised thioether macrocycles: synthesis of 1,5,9-trithiacyclododecane-3,7,11-triol $(HO)_3[12]aneS_3$

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**The tri-alcohol-functionalised trithioether macrocycle 1,5,9-trithiacyclododecane-3,7,11-triol $(HO)_3[12]aneS_3$, and its tri-anisate derivative have been synthesised, representing the first example of a thioether macrocycle functionalised on each backbone.**

The chemistry of thioether macrocycles is an area of chemistry that has received much attention over recent years because of the ability of these macrocycles to co-ordinate transition metal centres strongly and stabilise unusual oxidation states and geometries.[1] Functionalised thioether macrocycles have received growing attention but the difficulty of their synthesis has resulted in less rapid progress than their unfunctionalised analogues.[2–9] The most studied functionalised thioether macrocycles have been those with alcohol groups attached to their backbone and these have included *syn*/*anti*-$(HO)_2[14]aneS_4$ and *syn*/*anti*-$(HO)_2[16]aneS_4$,[3] $(HO)[14]aneS_4$,[3,4] $(HO)[10]aneS_3$,[5] $(HO)[11]aneS_3$,[5] $(HO)[12]aneS_3$,[5] $(HOCH_2)[9]aneS_3$,[6] $(HO)[19]aneS_6$ and $(HO)[20]aneS_6$ [7] (Fig. 1). Subsequent derivatisation of these alcohol groups *via* ester linkages has led to the formation of a range of ligands which exhibit liquid-crystalline behaviour,[8] or can be used as sensing devices.[9] Bearing these properties in mind, it is important to develop the synthetic strategies towards functionalised thioether macrocycles.[10] To this end we have synthesised the macrocycle $(HO)_3[12]aneS_3$ (Fig. 2), the first example of a thioether macrocycle functionalised on each backbone. This compound is particularly significant as it has three-fold symmetry, as would appropriately functionalised derivatives. Such targets are particularly significant for the development of potential new liquid-crystalline materials showing trigonal symmetry.

The triol $(HO)_3[12]aneS_3$ **6** was prepared using the route outlined in Scheme 1. Treatment of sodium benzylthiolate with epichlorohydrin in EtOH gave the thioether-substituted epoxide **1**,[11] which was then treated with $Na_2S \cdot 9H_2O$ to afford the trithioether **2** (79%). Compound **2** was purified by column chromatography (silica, $CH_2Cl_2$) to remove impurities of 1,9-bis(benzyl)-3-hydroxy-1,5-dithiapentane. In order that deprotection of the benzyl groups from the terminal thioethers proceeded successfully, the alcohol groups were protected. This was achieved by using tetrahydropyranyl groups introduced by reacting **2** with dihydropyran in the presence of catalytic amounts of PPTS (pyridinium *p*-tosylate)[12] to yield compound **3** (90%). Treatment of **3** with Na–$NH_3$ led to cleavage of the benzyl groups to afford the dithiol **4** (78%). Cyclisation of **4** with tetrahydropyranyl protected 1,3-dichloro-2-propanol, **5**, under high-dilution conditions in DMF in the presence of $Cs_2CO_3$ gave the functionalised $[12]aneS_3$ analogue compound **6** (63%). Owing to the chiral centres in the tetrahydropyranyl groups, as well as the two possible isomers of the $(RO)_3[12]aneS_3$ macrocyclic core, compound **6** exists as 12 possible isomers. Attempts to separate any of the isomers by column chromatography proved unsuccessful and thus **6** was characterised as a mixture of these isomers leading to complex $^1H$ and $^{13}C\{^1H\}$ NMR spectra. Treatment of **6** (as a mixture of isomers) with concentrated HCl in THF–MeOH afforded $(HO)_3[12]aneS_3$ **7**, isolated as a colourless crystalline product consisting of a mixture of two isomers (57%).

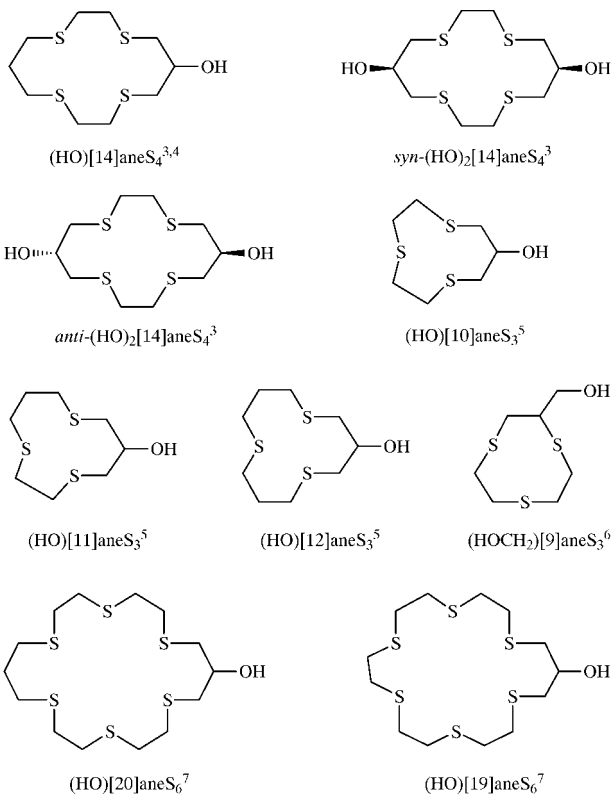



**Fig. 1** Examples of previously reported examples of alcohol-functionalised thioether macrocycles.

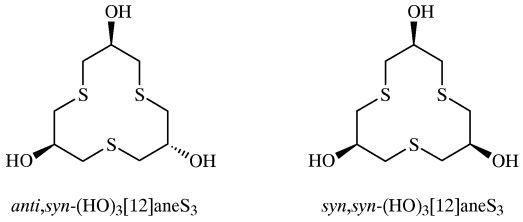
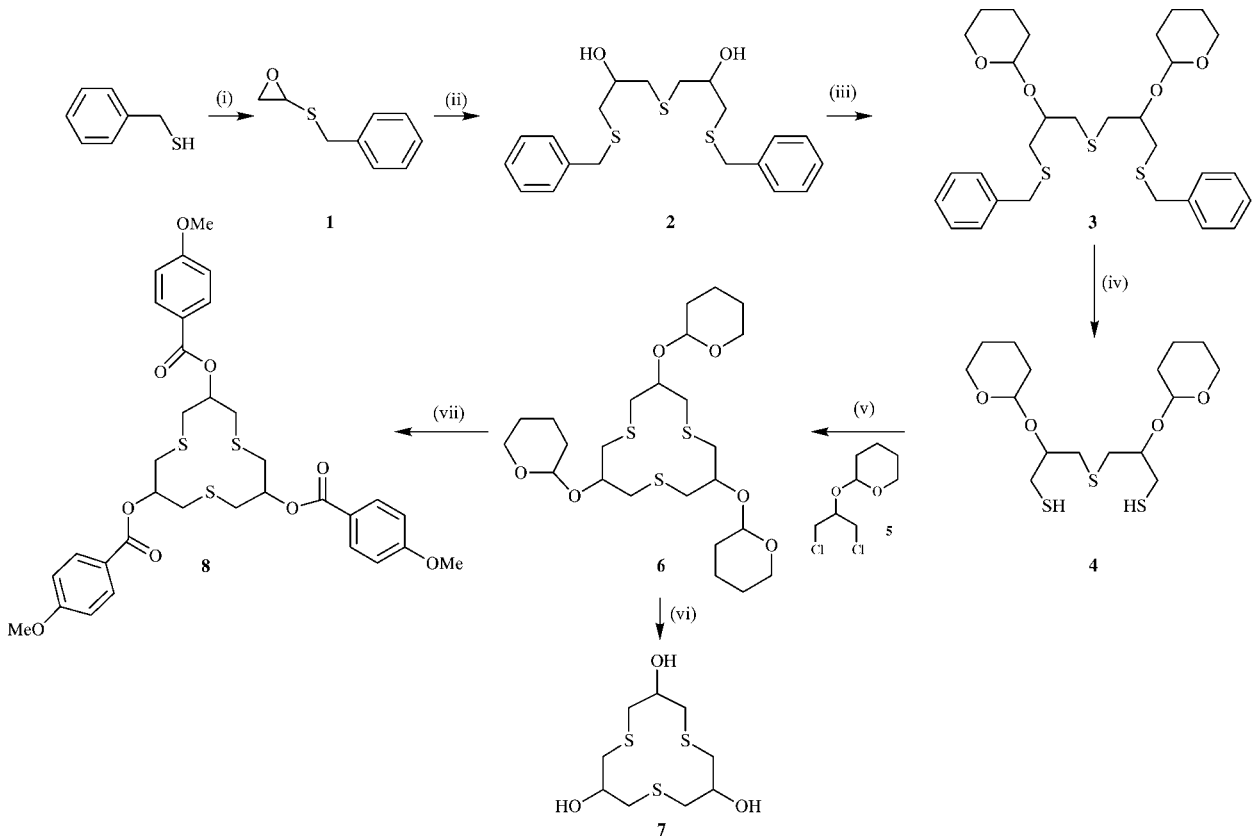


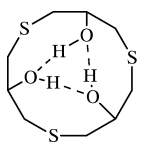

**Fig. 2** The *anti*,*syn* and *syn*,*syn* isomers of $(HO)_3[12]aneS_3$.



**Scheme 1** Synthetic route for the preparation of $(HO)_3[12]aneS_3$; (i) NaOEt (+/−)epichlorohydrin;[11] (ii) $Na_2S \cdot 9H_2O$; (iii) dihydropyran, PPTS (pyridinium *p*-tosylate), $CH_2Cl_2$;[12] (iv) Na–$NH_3$; (v) $Cs_2CO_3$, DMF, 65 °C; (vi) HCl, MeOH–THF; (vii) 4-methoxybenzoyl chloride, 4-methoxybenzoic acid, THF.

As illustrated in Fig. 2 $(HO)_3[12]aneS_3$ has two different isomeric forms, *syn,syn* and *anti,syn*. The *anti,syn* isomer is favoured on a statistical basis, when using racemic epichlorohydrin to prepare compound **1**, which should give a 3 : 1 excess of this isomer in comparison to the *syn,syn* form. Confirmation that the isomers were prepared in the statistically predicted ratio was born out by the $^1H$ NMR spectrum of isolated samples of $(HO)_3[12]aneS_3$. Recrystallisation of $(HO)_3[12]aneS_3$ from ethanol can be used to isolate the *anti,syn* isomer in greater than 98% purity, due to the greater solubility of the *syn,syn* isomer in this solvent. The *anti,syn* isomer can therefore be isolated in high purity: however the purification of the minor, more soluble *syn,syn* isomer is limited by the quantities of product isolated. On these small scales, the *syn,syn* isomer is always isolated with some *anti,syn* contamination.

Esterification of **7** proved extremely difficult under a variety of conditions providing no evidence for the formation of triester functionalised $[12]aneS_3$ units. This is in agreement with our previous experience with mono-ol and diol-substituted macrocyclic species. For example the reaction between $(HO)[14]aneS_4$ and aryl acid chlorides in the presence of 4-dimethylaminopyridine (DMAP)–$NEt_3$ proceeds in typically 80% yield[13] whereas the diesterification of $(HO)_2[14]aneS_4$ under similar conditions affords approximately 50% of the desired product.[8] This reduction in yield of the desired product might be accounted for by the possibility of intramolecular hydrogen-bonding in $(HO)_2[14]aneS_4$ which will inhibit the esterification reaction. This problem would be accentuated in $(HO)_3[12]aneS_3$ **7** as there is clear potential for the formation of three intra-molecular hydrogen-bonds severely limiting deprotonation of the alcoholic groups (Scheme 2). Indeed, metal-free thioether crowns are well established to incorporate exocyclic S-donors,[1] thus facilitating endocyclic hydrogen-bonding in polyfunctionalised alcohol and especially alkoxide derivatives.



**Scheme 2** Schematic representation of potential intra-molecular hydrogen-bonding in $(HO)_3[12]aneS_3$.

We attempted to circumvent this problem by direct esterification of **6** [14] which does not have the possibility for intramolecular hydrogen-bonding. The reaction of **6** with 4-methoxybenzoic acid and 4-methoxybenzoyl chloride in THF should proceed *via* sequential deprotection of tetrahydropyranyl units followed by esterification thus avoiding any potential problems with internal hydrogen-bonding. The reaction does indeed afford the desired tri-esterified product **8** but only in 3% yield. Macrocycle **8** was isolated as a single isomer (*anti,syn*) but the low yield of the reaction suggests that the possible formation of the *syn,syn* isomer should not be discounted.

We are currently pursuing the further development of the chemistry of $(HO)_3[12]aneS_3$ and related systems for the development of new liquid-crystalline materials.

## Experimental

All NMR experiments were performed on a Bruker DPX300 spectrometer operating at 300 MHz ($^1H$) or 75.5 MHz ($^{13}C$). Elemental analytical data were obtained by the microanalytical service (Perkin–Elmer 240B analyser) at the University of Nottingham. Starting materials were purchased from Aldrich Chemicals and were used without further purification.

### 1,9-Bis(benzyl)-3,7-dihydroxy-1,5,9-trithianonane 2

Sodium metal (1.27 g, 0.055 mol) was dissolved in EtOH (50 $cm^3$) to give a solution of NaOEt. To this solution was added benzylthiol (7.58 g, 0.060 mol) at 0 °C and the mixture stirred

for 1 h. This solution was then added dropwise to a solution of (+/−)epichlorohydrin (5.65 g, 0.060 mol) in EtOH (50 $cm^3$) at 0 °C with stirring under $N_2$. The mixture was allowed to warm to room temperature and stirred for a further hour. To this was added $Na_2S \cdot 9H_2O$ (7.20 g, 0.030 mol) and the suspension stirred overnight. The solution was hydrolysed by adding water (50 $cm^3$) and extracted into $CH_2Cl_2$ (3 × 50 $cm^3$) and the organic layer dried over $MgSO_4$. The organic fraction was reduced to give a viscous pale yellow oil which was purified using column chromatography (silica, $CH_2Cl_2$) $R_f = 0.30$; (79%). NMR: $^1H$ ($CDCl_3$), $\delta$ 7.35–7.25 (10H, m, C*H* of Ph), 3.77–3.73 [6H, m, C*H*(OH), C$H_2$Ph], 3.2 (2H br s, $CH_2OH$), 2.8–2.5 (8H, m, C$H_2$S); $^{13}C$-{$^1H$} ($CDCl_3$), $\delta$ 138.1, 129.0, 128.7, 127.2 (*C*H, Ph); 69.7, 69.0, 66.8 [*C*H(OH)]; 39.1, 37.6, 36.8 (*C*$H_2$S, *C*$H_2$Ph); MS $m/z^+$ (M − $CH_2$Ph) 303; $C_{20}H_{26}O_2S_3$ requires C, 60.9; H, 6.6; obtained C, 60.3, H, 6.9%.

### 1,9-Bis(benzyl)-3,7-bis(tetrahydropyranyloxy)-1,5,9-trithianonane 3

To a solution of **2** (3.15 g, 8 mmol) in $CH_2Cl_2$ (30 $cm^3$) was added 3 equivalents of dihydropyran (2.01 g, 0.024 mol) and pyridinium tosylate (PPTS) (10 mg). This mixture was stirred overnight and the solvent removed under vacuum to give a pale yellow oil. The compound was purified using column chromatography (silica, $CH_2Cl_2$) $R_f = 0.45$; (90%). NMR: $^1H$ ($CDCl_3$), $\delta$ 7.25–7.35 (10H, m C*H* of Ph), 4.68–4.65 [2H, m, C*H*(OR)(OR′)], 4.00–3.85 (4H, m SC$H_2$Ph), 3.77–3.73 (4H, m, C$H_2$O), 3.50–3.40 [2H, m C*H*(OR)], 2.90–2.60 (8H, m, C$H_2$S), 1.90–1.50 (12H, m, C$H_2$C$H_2$C$H_2$, THP); $^{13}C$-{$^1H$} ($CDCl_3$), $\delta$ 128.9, 128.4, 126.9 (*C*H, Ph); 98.4 [*C*H(OR)(OR′)]; 75.9 [*C*$H_2$OR)]; 62.6 [*C*H(OR)]; 37.0, 35.7, 34.3 (*C*$H_2$S, S*C*$H_2$Ph); 30.8, 25.4, 19.6 (*C*$H_2$*C*$H_2$*C*$H_2$ of THP); MS $m/z^+$ (M − $CH_2$Ph) 471; $C_{30}H_{42}O_4S_3$ requires C, 64.1; H, 7.5; obtained C, 64.3; H, 7.6%.

### 3,7-Bis(tetrahydropyranyloxy)-5-thiadecane-1,9-dithiol 4

Liquid $NH_3$ (*ca.* 50 $cm^3$) was condensed into a solution of **3** (1.50 g, 0.25 mmol) in thf (20 $cm^3$) at −78 °C, under a stream of $N_2$. To this was added Na metal (0.25 g, 0.01 mol, 4 equivalents) and the mixture was stirred until a permanent deep blue colour was produced. The reaction mixture was stirred for a further 30 min and the blue colour dissipated by addition of an excess of $NH_4Cl$. The reaction mixture was warmed to room temperature allowing evaporation of the liquid ammonia and the reaction mixture hydrolysed by addition of water (50 $cm^3$). This mixture was then washed with $CH_2Cl_2$ (3 × 25 $cm^3$) and the water layer acidified to *ca.* pH 4 with HCl (2 mol $dm^{-3}$). This acidic solution was extracted with $CH_2Cl_2$ (3 × 25 $cm^3$) and the organic layer dried over $MgSO_4$ under $N_2$. The organic layer was then reduced in volume to give a pale yellow oil (78%) which was used without further purification. Compound **4** was stored under $N_2$ at −10 °C. NMR: $^1H$ ($CDCl_3$), $\delta$ 4.70 [2H, br t, C*H*(OR)(OR′)], 3.93–3.86 (4H, m, C$H_2$O), 3.53 [2H, m, C*H*(OR)], 2.9–2.6 (8H, m, C$H_2$S), 1.9–1.5 (12H, m, C$H_2$C$H_2$C$H_2$ of THP); $^{13}C$-{$^1H$} ($CDCl_3$), $\delta$ 99.0 [*C*H(OR)(OR′)]; 77.6 [*C*H(OR)]; 63.3 [*C*$H_2$(OR)]; 36.6, 35.5 (*C*$H_2$S); 31.2, 25.7, 20.1 (*C*$H_2$*C*$H_2$*C*$H_2$, THP); MS $m/z^+$ 382.

### 1,3-Dichloro-2-tetrahydropyranyloxypropane 5

To a solution of 1,3-dichloropropan-2-ol (3.00 g, 0.023 mol) in $CH_2Cl_2$ (30 $cm^3$) was added 1.5 equivalents of dihydropyran (2.90 g, 0.034 mol) and pyridinium *p*-tosylate (10 mg). This mixture was stirred overnight and the solvent removed under vacuum to give a pale yellow oil. The compound was purified by washing through a silica pad with $CH_2Cl_2$; (80%). NMR: $^1H$ ($CDCl_3$), $\delta$ 4.80 [1H, m, C*H*(OR)(OR′)], 4.1–3.5 [7H, m, C$H_2$O, C$H_2$Cl, C*H*(OR)], 1.9–1.5 (6H, m, C$H_2$C$H_2$C$H_2$ of THP); $^{13}C$-{$^1H$} ($CDCl_3$), $\delta$ 99.0 [*C*H(OR)(OR′)]; 76.0 [*C*H(OR)]; 62.7 [*C*$H_2$(OR)]; 44.3, 43.4 (*C*$H_2$Cl); 30.5, 25.5, 19.3 (*C*$H_2$*C*$H_2$*C*$H_2$ of THP); MS $m/z^+$ (M − H), 211, HRMS ($C_8H_{13}O_2{}^{35}Cl_2$) 211.03017; $C_8H_{14}O_2Cl_2$ calculated C, 45.1; H, 6.6; obtained C, 45.1; H, 6.9%.

### 3,7,11-Tris(tetrahydropyranyloxy)-1,5,9- trithiacyclododecane 6

To a stirred suspension of $Cs_2CO_3$ (1.167 g, 3.58 mmol) in DMF (400 $cm^3$) at 65 °C, under $N_2$, was added a solution of **4** (0.679 g, 1.79 mmol) and **5** (0.380 g, 1.79 mmol) in DMF (250 $cm^3$) over a period of 24 h. The solution was stirred for a further 2 h and then allowed to cool to room temperature. The DMF was removed by rotary evaporation to give a yellow oil. This crude product was purified by column chromatography (silica, $CH_2Cl_2$, $R_f = 0.3$) to give the product as a viscous yellow oil (63%). NMR: $^1H$ ($CDCl_3$), $\delta$ 4.85–4.70 [3H, m, C*H*(OR)(OR′)], 4.05–3.85 (6H, m, C$H_2$O), 3.50–3.40 [3H, m, C*H*(OR)], 3.30–2.40 (12H, m, C$H_2$S), 1.9–1.5 (18H, m, C$H_2$C$H_2$C$H_2$ of THP); $^{13}C$-{$^1H$} ($CDCl_3$), $\delta$ 100.8, 100.4, 99.9, 99.5, 99.1, 98.45, 98.3, 97.8 [*C*H(OR)(OR′)]; 77.7, 77.6, 77.4, 76.1, 74.2, 74.1, 73.9, 73.8, 72.1, 71.9, 71.7, 71.3 [*C*H(OR)]; 63.1, 63.0, 62.8, 62.4 [*C*$H_2$(OR)]; 37.3, 37.2, 36.6, 36.5, 36.0, 35.8, 35.5, 35.1, 34.9, 34.5, 33.9, 33.7, 33.6, 33.1, 32.9, 32.8, 32.6 (*C*$H_2$S); 31.1, 30.9, 25.8, 20.0, 19.8, 19.5 (*C*$H_2$*C*$H_2$*C*$H_2$, THP); HRMS 522.21234 ($C_{24}H_{42}O_6S_3$ requires 522.21436).

### 1,5,9-Trithiacyclododecane-3,7,11-triol 7

To a solution of **5** (113 mg) in MeOH (5 $cm^3$) and THF (5 $cm^3$) was added concentrated HCl (0.5 $cm^3$). This solution was stirred overnight and then all the solvent removed under vacuum. The crude yellow oil was recrystallised from hot EtOH to give the product as colourless crystals (57%). MS $m/z^+$ 270; $C_8H_{14}O_2Cl_2$ requires C, 40.0; H, 6.7; obtained C, 39.5; H, 6.9%. NMR: *anti,syn* isomer: $^1H$ ($CD_3OD$), $\delta$ 4.06 [1H, m, C*H*(OH)], 3.95–3.93 [2H, m, C*H*(OH)], 3.3–3.2 (4H, m, C$H_2$S), 3.0–2.8 (4H, m, C$H_2$S), 2.5–2.4 (4H, m, C$H_2$S); $^{13}C$-{$^1H$} ($CD_3OD$), $\delta$ 67.9, 65.7 [*C*H(OH)]; 37.2, 35.2, 33.7 (*C*$H_2$S). *syn,syn* isomer: $^1H$ ($CD_3OD$), $\delta$ 3.95–3.93 [3H, m, C*H*(OH)], 3.4–3.3 (6H, m, C$H_2$S), 2.9–2.7 (6H, m, C$H_2$S); $^{13}C$-{$^1H$} ($CD_3OD$), $\delta$ 72.0 [*C*H(OH)]; 38.6 (*C*$H_2$S).

### 1,5,9-Trithiacyclododecane-3,7,11-triyl trianisate 8

To a solution of **5** (261 mg, 0.5 mmol) in THF (30 $cm^3$) was added 6 molar equivalents of 4-methoxybenzoyl chloride (511 mg, 3.0 mmol) and 6 molar equivalents of 4-methoxybenzoic acid (456 mg, 3.0 mmol). The solution was refluxed for 16 h under $N_2$ and then all the solvent was removed under vacuum. The crude product was purified by column chromatography (silica, $CH_2Cl_2$, $R_f = 0.2$) to give the product as a colourless solid following removal of the solvent (3%). NMR: $^1H$ ($CDCl_3$) $\delta$ (*anti,syn*) 8.06 [6H, dd, $J = 9$Hz, C*H* of anisate], 6.96 [6H, dd, $J = 9$Hz, C*H* of anisate], 5.60 [1H, m, C*H*(OR)], 5.46 [2H, m, C*H*(OR)], 3.88 (9H, m, C$H_3$), 3.73–3.62 (2H, m, C$H_2$S), 3.25–3.18 (4H, m, C$H_2$S), 3.07–3.00 (2H, m, C$H_2$S), 2.89–2.75 (4H, m, C$H_2$S); $^{13}C$-{$^1H$} ($CDCl_3$) DEPT (135 °C), $\delta$ 131.8 [*C*H of anisate], 113.78 [*C*H of anisate], 69.2 [*C*H(OR)], 68.1 [*C*H(OR)], 55.48 [*C*$H_3$, OMe], 34.1(*C*$H_2$S), 32.9 (*C*$H_2$S), 31.2 (*C*$H_2$S).

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## References

1 A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1; S. R. Cooper and S. C. Rawle, *Struct. Bonding* (*Berlin*), 1990, **72**, 1; J. P.

Danks, N. R. Champness and M. Schröder, *Coord. Chem. Rev.*, 1998, **174**, 417 and refs. therein.
2 J. Buter, R. M. Kellogg and F. van Bolhuis, *J. Chem. Soc., Chem. Commun.*, 1991, 910; J. J. H. Edema, J. Buter, F. S. Schoonbeek, A. Meetsma, F. van Bolhuis and R. M. Kellogg, *J. Org. Chem.*, 1993, **58**, 5624; Addition/correction, *J. Org. Chem.*, 1994, **59**, 3242; J. J. H. Edema, M. Hoogenraad, R. M. Kellogg, H. Kooijman and A. L. Spek, *J. Org. Chem.*, 1993, **58**, 5282; J. J. H. Edema, J. Buter, F. S. Schoonbeek, R. M. Kellogg, F. van Bolhuis and A. L. Spek, *Inorg. Chem.*, 1994, **33**, 2448; J. J. H. Edema, H. T. Stock, J. Buter, R. M. Kellogg, W. J. J. Smeets, A. L. Spek and F. van Bolhuis, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 436; J. J. H. Edema, J. Buter, R. M. Kellogg, A. L. Spek and F. van Bolhuis, *J. Chem. Soc., Chem. Commun.*, 1992, 1558; J. Buter, R. M. Kellogg and F. van Bolhuis, *J. Chem. Soc., Chem. Commun.*, 1990, 282; B. K. Vriesema, M. Lemaire, J. Buter and R. M. Kellogg, *J. Org. Chem.*, 1986, **51**, 5169.
3 V. B. Pett, G. H. Leggett, T. H. Cooper, P. R. Reed, D. Situmeang, L. A. Ochrymowycz and D. B. Rorabacher, *Inorg. Chem.*, 1988, **27**, 2164.
4 H. Kakiuchi, M. Tomoi, O. Abe and K. Kihara, *Jpn. Kokai Tokkyo Koho*, 80 19 221, Feb. 9, 1980; *Chem. Abstr.*, 1980, **93**, 72924x; K. Saito, I. Taninaka, S. Murakami and A. Muromatsu, *Anal. Chim. Acta*, 1994, **299**, 137; K. Yamashita, K. Kurita, K. Ohara, K. Tamura, M. Nango and K. Tsuda, *React. Funct. Polym.*, 1996, **31**, 47.
5 W. N. Setzer, E. L. Cacioppo, Q. Guo, G. J. Grant, D. D. Kim, J. L. Hubbard and D. G. VanDerveer, *Inorg. Chem.*, 1990, **29**, 2672; W. N. Setzer, S. Afshar, N. L. Burns, L. A. Ferrante, A. M. Hester, E. J. Meehan, Jr., G. J. Grant, S. M. Isaac, C. P. Laudeman and D. G. VanDerveer, *Heteroat. Chem.*, 1990, **1**, 375.
6 R. J. Smith, G. D. Adams, A. P. Richardson, H.-J. Kuppers and P. J. Blower, *J. Chem. Soc., Chem. Commun*, 1991, 4475; R. J. Smith, S. N. Salek, M. J. Went, P. J. Blower and N. J. Barnard, *J. Chem. Soc., Dalton Trans.*, 1994, 3165.
7 R. Alberto, W. Nef, A. Smith, T. A. Kaden, M. Neuberger, M. Zehnder, A. Frey, U. Abram and P. A. Schubiger, *Inorg. Chem.*, 1996, **35**, 3420.
8 A. J. Blake, D. W. Bruce, I. A. Fallis, S. Parsons and M. Schroder, *J. Chem. Soc., Chem. Commun.*, 1994, 2471; A. J. Blake, D. W. Bruce, I. A. Fallis, S. Parsons, H. Richtzenhain, S. A. Ross and M. Schroder, *Philos. Trans. R. Soc. London, A*, 1996, **354**, 395.
9 G. De Santis, L. Fabrizzi, M. Licchelli, C. Mangano and D. Sacchi, *Inorg. Chem.*, 1995, **34**, 3581; G. De Santis, L. Fabrizzi, M. Licchelli, C. Mangano, D. Sacchi and N. Sardone, *Inorg. Chim Acta*, 1997, **257**, 69.
10 L. R. Sutton, A. J. Blake, P. A. Cooke, R. O. Gould, M. S. Jackson, S. Parsons and M. Schröder, *Synlett*, 1999, in the press.
11 U. Sulser, J. Widmer and H. Goeth, *Helv. Chim. Acta*, 1977, **60**, 1676.
12 M. Miyashita, A. Yoshikoshi and P. A. Grieco, *J. Org. Chem.*, 1977, **42**, 3772.
13 A. J. Blake, D. W. Bruce, M. Schröder and L. R. Sutton, unpublished work.
14 T. Bakos and I. Vincze, *Synth. Commun.*, 1989, **19**, 523.

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