Co-ordination Complexes containing Multidentate Ligands. Part VIII.[1] Synthesis of Three Bis(*o*-methylthiophenylthio)alkanes and their Reactions with Cobalt(II), Nickel(II), Copper(II), Palladium(II), Platinum(II), and Rhodium(III) Salts

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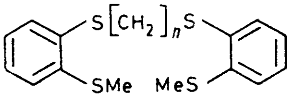
Three open-chain quadridentate thioether ligands, 1,2-bis(*o*-methylthiophenylthio)ethane, 1,3-bis(*o*-methylthiophenylthio)propane, and 1,4-bis(*o*-methylthiophenylthio)butane, have been prepared and their complexes with cobalt(II), nickel(II), copper(II), palladium(II), platinum(II), and rhodium(III) salts isolated and characterised. These are mainly of the types six-co-ordinate $[MLX_2]$ (M = Co or Ni) in which the ligand is quadridentate, four-co-ordinate $[M_2LX_4]$ (M = Cu, Pd, or Pt) in which the ligand is bridging quadridentate, and $[Rh_4L_3X_{12}]$. The behaviour of these ligands is discussed in terms of normal metal co-ordination numbers and their inability to compete with halides for co-ordination positions. In *NN*-dimethylformamide the Pd^{II} and Pt^{II} complexes undergo complicated *S*-dealkylation reactions. With the former three products have been identified and contain the ligands *o*-methylthiobenzenethiolate and benzene-1,2-dithiolate.

DURING the last decade there has been a good deal of interest in the synthesis and complex formation of multidentate ligands containing heavy donor atoms (ref. 2 is a recent review). These have mainly been of the tripod quadridentate type and the trigonal symmetry of these ligands most frequently gives rise to trigonal-bipyramidal complexes with d^7 and d^8 metal ions.[3] More recently interest has grown in linear or open-chain quadridentate ligands,[4] and these are in many respects more interesting than the tripod type, not least because their flexibility allows metal ions a good deal of freedom in adopting a particular geometry; thus planar,[5] square-pyramidal,[6] trigonal-bipyramidal,[5] and octahedral[7] arrangements are known for complexes of open-chain ligands.

We report here the synthesis of three open-chain tetrathioether ligands: 1,2-bis(*o*-methylthiophenylthio)ethane (bme); 1,3-bis(*o*-methylthiophenylthio)propane (bmp); and 1,4-bis(*o*-methylthiophenylthio)butane (bmb). Although there is a previous report of a tetrathioether,[8] this type of ligand is rare and the recent interest in metal-catalysed *S*-dealkylation reactions[9] has stimulated us to examine such reactions with these ligands. *S*-Dealkylations are almost invariably catalysed by heavy transition metals under forcing conditions, but a recent report[10] has shown that structurally similar ligands to these reported here, 1,2-bis(*o*-diphenylarsinophenylthio)ethane and analogues, undergo bis(*S*-dealkylation) on reaction with nickel(II) salts under mild conditions.



bme $n = 2$
bmp $n = 3$
bmb $n = 4$

EXPERIMENTAL

Preparation of the Ligands.—*o*-Methylthiobenzenethiol[11] (38.5 g, 0.247 mol) was added under nitrogen to sodium (5.7 g, 0.246 g-atom) in absolute ethanol (250 cm³) and stirred for 30 min. The appropriate α,ω-dihalogenoalkane (0.122 mol) was added slowly to the refluxing solution over 1 h during which time a white precipitate formed. The ethanol was removed on a rotory evaporator, the product extracted with dichloromethane, filtered, and the filtrate evaporated. Recrystallisation from $EtOH-CH_2Cl_2$ produced white crystalline products: 1,2-*bis*(o-*methylthiophenylthio*)*ethane* (bme), m.p. 99.5 °C (75%), δ 2.43 (CH_3), 3.08 (CH_2CH_2), and 7.13 p.p.m. (phenyl) (Found: C, 56.9; H, 5.3; S, 37.7. $C_{16}H_{18}S_4$ requires C, 56.8; H, 5.4; S, 37.9%); 1,3-*bis*(o-*methylthiophenylthio*)*propane* (bmp), m.p. 78 °C (80%), δ 2.45 (CH_3), 3.02 ($CH_2CH_2CH_2$), 1.9 ($CH_2CH_2CH_2$), and 7.15 p.p.m. (phenyl) (Found: C, 57.8; H, 5.7; S, 36.6. $C_{17}H_{20}S_4$ requires C, 57.9; H, 5.7; S, 36.4%); and 1,4-*bis*(o-*methylthiophenylthio*)*butane* (bmb), m.p. 108 °C

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(85%), δ 2.45 (CH_3), 2.9 ($CH_2CH_2CH_2CH_2$), 1.8 (CH_2CH_2-CH_2CH_2), and 7.15 p.p.m. (phenyl) (Found: C, 58.8; H, 6.4; S, 34.8. $C_{18}H_{22}S_4$ requires C, 59.0; H, 6.0; S, 35.0%).

Preparation of the Complexes.—[1,3-*Bis*(o-*methylthiophenylthio*)*propane*]*palladium*(II) *diperchlorate*, [Pd(bmp)]-$[ClO_4]_2$. Sodium tetrachloropalladate(II) (0.59 g, 2.0 mmol) in ethanol (15 cm^3) was mixed with a solution of the ligand (0.35 g, 1.0 mmol) in dichloromethane (70 cm^3). A solution of lithium perchlorate (1.0 g, 10.0 mmol) in ethanol (30 cm^3) was added simultaneously and the mixture stirred for 1 h. The solution was evaporated to dryness and the *product* recrystallised from dichloromethane–ethanol (0.1 g, 15%).

$[Pd_2LCl_4]$ (L = bme, bmp, *or* bmb). Sodium tetrachloropalladate(II) (0.59 g, 2.0 mmol) in ethanol (15 cm^3) and a solution of the ligand (1.0 mmol) in dichloromethane (15 cm^3) were mixed. A precipitate formed rapidly and stirring was continued for 1 h. The solid was filtered off, washed with ethanol (5 cm^3) and water (35 cm^3) to remove sodium chloride, and again with ethanol (15 cm^3) and diethyl ether (20 cm^3), and dried *in vacuo*. Yields 80—85%. The derivatives $[Pd_2LX_4]$ (X = Br or I) were obtained similarly except that the $Na_2[PdCl_4]$ was stirred with NaX (5 mol) in ethanol for 0.5 h before addition of the ligand; $[Pt_2LX_4]$ complexes were prepared by analogous routes.

$[NiLI_2]$ (L = bme *or* bmp). Hydrated nickel(II) iodide (0.66 g, *ca.* 2.0 mmol) was dissolved in a minimum quantity of hot n-butanol. The solution was filtered and treated with a dichloromethane solution (70 cm^3) of the ligand (2.0 mmol). After stirring for 15 min the precipitated complex was filtered off, washed with dichloromethane, and dried *in vacuo* (*ca.* 90%). The complexes $[Ni(bme)Br_2]$ and $[Co(bme)I_2]$ were obtained by analogous methods.

[1,2-*Bis*(o-*methylthiophenylthio*)*ethane*]*tetrachlorodicopper*(II), $[Cu_2(bme)Cl_4]$. Anhydrous copper(II) chloride (0.27 g, 2.0 mmol) in ethanol (15 cm^3) and the ligand (0.34 g, 1.0 mmol) in dichloromethane (10 cm^3) were stirred together for 3 h, and the dark precipitate filtered off, rinsed with ethanol, dichloromethane, and diethyl ether, and dried *in vacuo*. The complexes $[Cu_2LBr_4]$ (L = bme or bmp) were prepared analogously.

$[Cu_2LX_2]$ (L = bme *or* bmp, X = Br; L = bme, X = I). The appropriate copper(I) halide (2.0 mmol) dissolved in concentrated hydrohalogenic acid (15 cm^3) and ethanol (15 cm^3) was filtered into a solution of the ligand (1.0 mmol) in dichloromethane (20 cm^3). The resulting precipitate was isolated and purified as above.

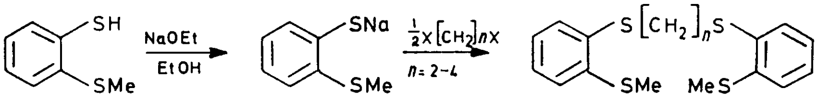
Tris[1,2-*bis*(o-*methylthiophenylthio*)*ethane*]*dodecahalogenotetrarhodium*(III), $[Rh_4(bme)_3X_{12}]$ (X = Cl, Br, *or* I). Rhodium(III) chloride (0.42 g, 2.0 mmol) in ethanol (15 cm^3) and a solution of the ligand (0.68 g, 2.0 mmol) in dichloromethane (15 cm^3) were stirred together for 1 h after which the precipitate was filtered off, washed with ethanol (15 cm^3) and dichloromethane (15 cm^3), and dried *in vacuo* (70—80%). The bromo- and iodo-complexes were prepared similarly except that $RhCl_3$ was stirred with NaX (5 mol) in ethanol for 0.5 h before addition of the ligand.

Dealkylation Reactions.—The $[Pd_2LX_4]$ complex (*ca.* 1.0 g) suspended in *NN*-dimethylformamide (dmf)–butanol (40 cm^3) (1 : 1) was heated under reflux until all the solid had dissolved, resulting in a dark red-brown solution (4—6 h). The solution was evaporated almost to dryness (2—3 cm^3) and after cooling the product was precipitated on addition of diethyl ether (50 cm^3). The product was filtered off and recrystallised from dichloromethane as brown (*ca.* 0.1 g) and black solids (*ca.* 0.7 g). Thin-layer chromatography (t.l.c.) showed at least three products to be present in the brown solid and these were separated using 8 × 8 in t.l.c. plates with a support medium of silica gel and dmf–chloroform (1 : 49) as eluant. The products were individually removed from the support by extraction into dmf and work-up in the usual manner.

Physical Measurements.—^1H N.m.r. measurements were made on a Varian Associates HA100 spectrophotometer in $CDCl_3$. All other physical measurements were made as previously described.[12]

RESULTS AND DISCUSSION

Ligands.—The three open-chain quadridentate thioether ligands were obtained by reaction (1). All three are white air-stable crystalline solids, essentially insoluble in ethanol but readily soluble in dichloromethane.



(1)

Nickel(II) *Complexes*.—Only $[Ni(bme)X_2]$ (X = Br or I) and $[Ni(bmp)I_2]$ were isolated pure, although slightly impure $[Ni(bmp)Br_2]$ was also obtained. These complexes were produced by reaction of the nickel(II) halide in the minimum amount of n-butanol with the ligand in excess of dichloromethane. They could not be prepared in stronger donor solvents (*e.g.* EtOH) which compete successfully with the thioether groups for co-ordination to Ni^{II}. Once formed the complexes are insoluble in all common solvents, except dmf in which they dissolve on heating, but rapidly decompose into $[Ni(dmf)_6]^{2+}$ and free ligand. Attempts to prepare di-chloro-, -isothiocyanato-, or -perchlorato-complexes were unsuccessful; the importance of the counter ion in stabilising these complexes is probably another example of symbiosis.[13]

The magnetic moments of the three complexes, $\mu_{eff.}$ = 2.9—3.0 B.M.,* indicate octahedral stereochemistry and this structure is confirmed by the reflectance spectra (Table). The appearance of only one ν(Ni–Br) band at 204 cm^{-1} in the i.r. spectrum of $[Ni(bme)Br_2]$ {and only one absorption for the slightly impure $[Ni(bmp)Br_2]$} suggests that these complexes have a *trans* structure, and we used Drago's treatment[14,15] to analyse the spectra for in-plane and out-of-plane ligand fields.

	Dq^{xy}/cm^{-1}	Dq^{z}/cm^{-1}
$[Ni(bme)Br_2]$	1 020	740
$[Ni(bme)I_2]$	1 030	730
$[Ni(bmp)I_2]$	1 030	750

As expected, these ligands appear to be spectrochemically

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* 1 B.M. ≈ 9.27×10^{-24} Am^2, 1M = 1 mol dm^{-3}.

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quite weak and weaker than the macrocyclic tetrathioether 1,4,8,11-tetrathiacyclotetradecane of Rosen and Busch which also forms *trans*-$[Ni(S_4)X_2]$ complexes (Dq^{xy} 1 070 cm^{-1}).[8]

Five-co-ordinate complexes of type $[NiLX]^+$ could not be formed; reaction of the ligands with NiX_2–$Ni[ClO_4]_2$ (X = Br or I) mixtures [16] resulted only in the formation of octahedral $[NiLX_2]$ complexes. In marked contrast to the interaction of NiX_2 with the structurally similar diarsine dithioether compounds,[10] these Ni^{II} complexes did not dealkylate on heating under reflux in acetone or n-butanol, whilst refluxing dmf decomposed the complexes and deposited the unchanged ligand.

Analytical and spectroscopic data for the complexes

Complex	Colour	Analyses/% Calc. C	H	Found C	H	$\mu_{eff.}$/B.M.	Reflectance spectra ($10^{-3}\,\bar{\nu}/cm^{-1}$)	I.r. spectra, $\bar{\nu}$(M–X)/cm^{-1}
$[Pd_2(bme)Cl_4]\cdot HOEt$	Yellow	29.2	3.2	28.8	3.0		25.8	328, 315
$[Pd_2(bme)Br_4]\cdot HOEt$	Orange	23.6	2.6	23.4	2.5		27.4 (sh), 24.4	258
$[Pd_2(bme)I_4]\cdot HOEt$	Maroon	19.6	2.1	19.7	2.0		27.8 (sh), 20.0	
$[Pd_2(bmp)Cl_4]$	Yellow	29.0	2.8	29.1	3.0		26.7	335, 318
$[Pd_2(bmp)Br_4]$	Orange	23.0	2.3	23.4	2.4		27.4 (sh), 24.1	250
$[Pd_2(bmp)I_4]$	Maroon	19.0	1.9	19.2	2.0		27.8 (sh), 25.3 (sh), 20.0, 17.4 (sh)	
$[Pd_2(bmb)Cl_4]$	Yellow	30.0	3.1	30.3	3.0		26.7, 25.3 (sh)	334, 315
$[Pd_2(bmb)Br_4]$	Orange	24.1	2.4	24.6	2.4		23.5	258
$[Pd_2(bmb)I_4]$	Maroon	20.0	2.0	20.2	1.9		26.3 (sh), 19.4, 18.2 (sh)	
$[Pt_2(bme)Cl_4]\cdot HOEt$	Cream	23.6	2.5	23.4	2.4		27.8 (sh)	335, 320
$[Pt_2(bme)Br_4]\cdot HOEt$	Pale yellow	19.8	2.2	20.2	2.1		26.3 (sh)	
$[Pt_2(bme)I_4]\cdot HOEt$	Yellow	16.8	1.9	16.9	1.9		25.3 (sh)	
$[Pt_2(bmp)Cl_4]$	White	23.0	2.3	23.0	2.5		21.7 (sh), 18.2 (sh)	325, 310
$[Pt_2(bmp)Br_4]$	Pale yellow	19.2	1.9	19.2	2.0		24.1 (sh), 20.6 (sh)	225
$[Pt_2(bmp)I_4]$	Yellow	16.3	1.6	16.7	1.7		25.6, 22.2 (sh)	
$[Pt_2(bmb)Cl_4]$	Cream	24.0	2.4	24.2	2.4			334, 320
$[Pt_2(bmb)Br_4]$	Lemon	20.5	2.0	20.5	2.1		26.7 (sh)	240
$[Pt_2(bmb)I_4]$	Yellow	17.1	1.7	17.2	1.8		26.3, 20.6 (sh)	
$[Ni(bme)Br_2]$	Emerald green	34.5	3.2	34.5	3.2	3.0	25.0 (sh), 16.1, 10,2, 8.85 (sh)	204
$[Ni(bme)I_2]$	Khaki	29.5	2.8	29.2	2.8	2.9	23.5, 20.6 (sh), 16.1, 10.3, 8.75	
$[Ni(bmp)I_2]\cdot CH_2Cl_2$	Dark brown	28.8	2.9	28.9	3.0	2.9	25.6, 20.2, 16.5, 10.3, 8.93 (sh)	
$[Cu_2(bme)Cl_4]\cdot HOEt$	Dark red	33.1	3.5	32.9	3.4	2.6	27.4 (sh), 20.0, 17.9 (sh), 11,2, 10.0	300, 266
$[Cu_2(bme)Br_4]\cdot HOEt$	Dark purple	26.0	2.9	25.8	2.8	2.4	27.8 (sh), 18.0, 17.0 (sh), 11.3, 10.8	240, 218
$[Cu_2(bmp)Br_4]\cdot HOEt$	Purple	27.0	3.1	26.8	3.0	2.6	27.4 (sh), 18.7, 16.7 (sh), 12.4	245, 210
$[Co(bme)I_2]\cdot 2CH_2Cl_2$	Black-purple	26.3	2.7	26.4	2.6	5.0	18.9 (sh), 18.0 (sh), 16.2, 14.2, 13.0	
$[Rh_4(bme)_3Cl_{12}]$	Yelow	31.1	2.9	30.8	3.4			
$[Rh_4(bme)_3Br_{12}]$	Orange	24.3	2.3	24.8	2.7			
$[Rh_4(bme)_3I_{12}]$	Red-brown	19.6	1.9	20.6	2.2			
$[Pd(bmp)][ClO_4]_2$	Yellow	31.0	3.0	30.9	3.1		27.8 (sh)	1 080, 620 *

* $[ClO_4]^-$ Absorptions.

The only cobalt(II) complex isolated was the relatively unstable $[Co(bme)I_2]\cdot 2CH_2Cl_2$. The i.r. spectrum of this complex was very similar to that of $[Ni(bme)I_2]$, implying a similar six-co-ordinate structure, and the magnetic moment of the former, $\mu_{eff.} = 5.0$ B.M., is confirmatory evidence.[17]

Palladium(II) *and Platinum*(II) *Complexes*.—In contrast to the wide range of structures and stoicheiometries formed by the diarsine dithioether compounds of Dutta *et al.*[18,19] with these metal ions, the present ligands form only one type of halogeno-complex with Pd^{II} and Pt^{II}. The reaction of $Na_2[MX_4]$ (M = Pd or Pt; X = Cl, Br, or I) with these ligands in 1 : 1, 2 : 1, or 1 : 2 molar ratios in a variety of organic solvents led only to immediate precipitation of $[M_2LX_4]$ complexes. These complexes are insoluble in all common organic solvents (other than boiling dmf). No reaction occurred between $Na_2[M(SCN)_4]$ complexes and these ligands, and it is worth noting that Goodall also failed to obtain thiocyanato-complexes of the spirocyclic $C(CH_2SR)_4$ ligands.[20]

The lower-energy visible-absorption bands (Table) are indicative of four- and not five-co-ordinate [21] complexes and the shift to lower energy in the order $Cl^- > Br^- > I^-$ indicates that the halides are co-ordinated. Absorptions due to $[MX_4]^{2-}$ ions [22] were absent, ruling out a formulation such as $[ML][MX_4]$. The far-i.r. spectra (400—200 cm^{-1}) were complex making assignment of ν(M–X) difficult. The frequencies of ν(M–X) (X = Cl or Br) (Table) are inconsistent with the presence of $[MX_4]^{2-}$ ions [23] or of *trans*-MX_2 arrangements,[24-26] but are in the range reported for *cis*-MX_2 moieties with *trans*-thioether donors.[24,27] Possible structures for these complexes are (I) and (II).

The reaction of bmp with $Na_2[PdCl_4]$ in the presence of

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[16] T. D. DuBois and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1395.

[17] R. Morassi, I. Bertini, and L. Sacconi, *Co-ordination Chem. Rev.*, 1973, **11**, 343.

[18] R. L. Dutta, D. H. Busch, and D. W. Meek, *Inorg. Chem.*, 1970, **9**, 2098.

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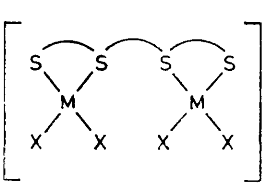
[25] R. J. H. Clarke, G. Natile, U. Belluco, L. Cattalini, and C. Filippin, *J. Chem. Soc.* (*A*), 1970, 659.

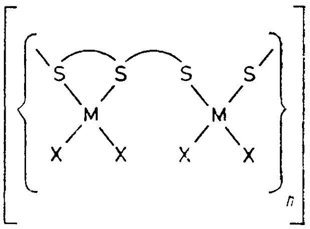
[26] B. E. Aires, J. E. Fergusson, D. T. Howarth, and J. M. Millar, *J. Chem. Soc.* (*A*), 1971, 1144.

[27] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

a large excess of Li[ClO_4] in EtOH–CH_2Cl_2 produced a small quantity of [Pd(bmp)][ClO_4]$_2$, which is a 1 : 2 electrolyte in nitromethane (Λ_M = 148 S cm^2 mol^{-1}, 10^{-3}M solution). The mull i.r. spectrum exhibited $\nu_3(ClO_4^-)$ at 1 080 cm^{-1} and as this band is broad and unsplit it is additional evidence that the perchlorate group is unco-ordinated.[28] The analogous complexes of bme and bmb could not be obtained.



(I)



(II)

The complexes [M_2LX_4] (M = Pd or Pt; L = bme, bmp, or bmb; X = Cl, Br, or I) underwent *S*-dealkylation reactions on prolonged reflux in dmf, the ease of dealkylation being Pd > Pt and bmb ~ bmp ≫ bme. The products of these reactions were complex and proved exceedingly difficult to separate and identify. The complexity arises from the number of possible sites of C–S bond fission; previous studies have been limited to ligands with only one or two possible sites for *S*-dealkylation.[9,10,18,19,29] In most cases we found that t.l.c. separation on silica gel using 2% dmf–$CHCl_3$ eluted three components [a further constituent(s) did not elute] in each case. In view of the complexity of the reactions only the [Pd_2(bmp)Cl_4] and [Pd_2(bmb)Cl_4] complexes were examined in detail. Yields were exceedingly small but attempts to increase these yields by extended reflux times produced metallic palladium. Elemental analyses (Pd, C, H, Cl, and S) of the products indicated them to be [PdL$'_2$], [PdL$'$Cl], and [PdL$''$]. The bidentate ligand L$'$ = *o*-methylthiobenzenethiolate is formed by loss of the trimethylene or tetramethylene backbone, and mass-spectral studies of the original bmp and bmb ligands showed that it is these C–S bonds which are easiest to cleave.[30] The pink [PdL$'_2$] complex is identical to that synthesised by Livingstone;[11] the [PdL$'$Cl] complex is a four-co-ordinate dimer, bridging chlorines being evidenced by the ν(Pd–Cl) band at 272 cm^{-1}.[31] The yellow-brown [PdL$''$] complex is undoubtedly polymeric *via* bridging sulphide links. There has been immense interest in ligands of type L$''$ (= benzene-1,2-dithiolate), usually derived from dithiolenes;[32] *in situ* synthesis from thioether compounds by *S*-dealkylation appears to be a novel route to this type of ligand. Unfortunately, attempts to identify the organic fragments derived from these *S*-dealkylation reactions were unsuccessful, possibly because of the known tendency of alkyl halides to react, at least partially, with dmf.[33] Attempts to promote dealkylation in other solvents (*e.g.* n-butanol) were unsuccessful.

Copper Complexes.—The reaction of copper(II) halides with bme and bmp produced [Cu_2(bme)X_4] (X = Cl or Br) and [Cu_2(bmp)Br_4]; neither [Cu_2(bmp)Cl_4] nor bmb complexes were isolable. The far-i.r. and electronic-reflectance spectra rule out the presence of [CuX_4]$^{2-}$ ions[34,35] and a [CuL][CuX_4] structure. Octahedral, tetrahedral, and planar geometries are known for copper(II) complexes[35] and are not readily distinguished by magnetic or spectroscopic studies. The magnetic moments of the complexes, $\mu_{eff.}$ = 2.4—2.6 B.M., are high for d^9 Cu^{II}, suggesting a large orbital contribution and hence a distorted environment about the metal. We tentatively propose a distorted-tetrahedral environment (with an S_2X_2 donor set about each Cu atom), although the large separation in ν(Cu–X) frequencies (Table) possibly suggests one bridging and one terminal X group, and hence a higher co-ordination number. Copper(II) perchlorate complexes could not be obtained and addition of ethanolic sodium iodide solution to Cu[ClO_4]$_2$–ligand mixtures in EtOH–CH_2Cl_2 produced a copper(I) complex and iodine. Thioether donors do not stabilise Cu^{II} iodo-complexes and thus differ from nitrogen bases such as 2,2$'$-bipyridyl.[36] Copper(I) complexes, [Cu_2LX_2] (L = bme or bmb; X = Br or I), were obtained by reaction of the ligand with the Cu^I halide dissolved in ethanol–conc. HX. Elemental analyses suggested that all these complexes were slightly contaminated with Cu^I halide and, as the [Cu_2LX_4] complexes are insoluble, purification was impossible.

Rhodium(III) *Complexes.*—Complexes of empirical formula [Rh_4(bme)$_3X_{12}$] (X = Cl, Br, or I) were readily precipitated from solutions of RhX_3 and bme, irrespective of the ratio of metal salt : ligand used. These are probably six-co-ordinate, thus accommodating the 24 donors on the four metal atoms. Insolubility hindered further study.

Conclusion.—Several factors are evident in determining the type of complex formed by these tetrathioether ligands. First, the ' normal ' co-ordination number (six for Ni^{II} with weak donor ligands, four for Pd^{II} and Cu^{II}, and six for Rh^{III}) of the metal ions seems to be important, and these co-ordination numbers persist in the complexes. Secondly, within the limits of these co-ordination numbers, metal–halogen co-ordination is dominant over metal–thioether. Thus in the four-co-ordinate complexes we find that we do not obtain [ML]X_2 but rather [M_2LX_4], *i.e.* for full binding of all donors the ligands are forced to bridge rather than either displace co-ordinated halide or increase the co-ordination number to six. Thus

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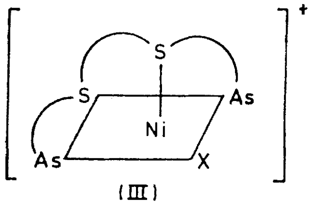
the ligands are quadridentate in the Ni^{II} complexes where six-co-ordination allows both halide and ligand full co-ordination. This tendency is even more marked in the Rh^{III} complexes where, in order to provide donor sites for all thioethers and halides, the stoicheiometry [$Rh_4L_3X_{12}$] rather than, say, [$RhLX_2$]X is obtained. Only in one case, [Pd(bmp)][ClO_4]$_2$, was it possible to obtain quadridentate chelation to a normally four-co-ordinate metal ion, and this was obtained only with [ClO_4]$^-$ counter ions and in very small yield. Thirdly, it may be pointed out that, although a survey of the complexes isolated suggests that the number of carbon atoms in the intermediate chelate chain (2, 3, and 4) plays a role in determining the ease of complex formation and isolation, this is undoubtedly a complicated factor and needs more study. Finally, the fact that quite forcing conditions (refluxing dmf) are needed to induce *S*-dealkylation reactions of the palladium and platinum complexes (and why no such reaction occurs for the nickel complexes) may shed some light on the surprisingly facile bis(*S*-dealkylation) reactions of the structurally similar diarsine dithioether compounds, bis(*o*-diphenylarsinophenyl)alkanes, catalysed by Ni^{II} salts.[10] In the nickel, palladium, and platinum complexes reported here all the evidence suggests that all four thioether donors co-ordinate in the same plane, whereas in the interaction of Ni^{II} salts with the diarsine compounds [10] it is suggested by molecular-model constructions that the five-co-ordinate complex formed has structure (III),[4] and it may well be that the peculiar conformation of the sulphur atoms is important in the ease of C–S bond fission.



(III)

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