The Chemistry of Sulphur–Nitrogen Ligands. Part I. Complex-formation and Dealkylation Reactions of 1,9-Bis(tritylthio)- and 1,9-Bis(benzylthio)-3,7-diazanonane in the Presence of Metal(II) Salts, and the Synthesis of Dibromo{3,13-dithia-6,10-diazabicyclo[13.4.0]nonadeca-1(15),16,18-triene}nickel(II)

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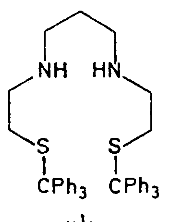
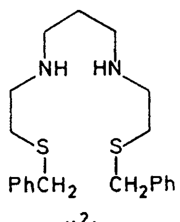
The quadridentate N_2S_2 donor ligands 1,9-bis(tritylthio)-3,7-diazanonane (L^1) and 1,9-bis(benzylthio)-3,7-diazanonane (L^2) have been prepared as their dihydrobromide salts and allowed to react with metal(II) acetates (M = Ni^{II}, Co^{II}, and Hg^{II}) in methanol solution. Both ligands react with Hg^{II} with concomitant dealkylation at the sulphur donor atoms to give a trinuclear complex $[Hg(HgL)_2]Br_2\cdot 3H_2O$ (L = 3,7-diazanonane-1,9-dithiolato). Treatment of this complex (dissolved in aqueous HCl) with H_2S gives the dihydrochloride of 3,7-diazanonane-1,9-dithiol. Dealkylation does not occur in the presence of Co^{II}, the isolated complexes in this case being blue tetrahedral $[CoL^1]Br_2$ and purple octahedral $[CoBr_2(L^2)]$. Nickel(II) gives the blue octahedral $[NiBr_2(L^2)]$, but catalyses rapid detritylation of L^1 to give the black, diamagnetic, trinuclear complex $[Ni(NiL)_2]Br_2$. Reaction of $[Ni(NiL)_2]Br_2$ with α,α′-dibromo-*o*-xylene in methanol solution gives blue dibromo{3,13-dithia-6,10-diazabicyclo[13.4.0]nonadeca-1(15),16,18-triene}nickel(II).

THE chemistry of sulphur–nitrogen chelating agents has been recently reviewed.[1] Many examples are known of *S*-dealkylation [1–6] of co-ordinated thioethers and of *S*-alkylation [1,7,8] of co-ordinated thiolato-ligands. *S*-Alkylation has been used for the preparation of macrocyclic nickel complexes.[8] The present paper discusses some aspects of the chemistry of the ligands 1,9-bis(tritylthio)-3,7-diazanonane (L^1) and 1,9-bis(benzylthio)-3,7-diazanonane (L^2). The benzyl and trityl functions are good leaving groups, so that ready dealkylation of some of the metal complexes would be expected giving metal complexes of 3,7-diazanonane-1,9-dithiol (L^3). The dihydrochloride of this ligand has been prepared by conventional organic routes by Felder and Bianchi.[9] *S*-Alkylation of suitable metal complexes of this ligand with reagents such as α,α′-dibromo-*o*-xylene should give complexes of the previously unknown macrocyclic ligand 3,13-dithia-6,10-diazabicyclo[13.4.0]nonadeca-1(15),16,18-triene (L^4).



(L^1)



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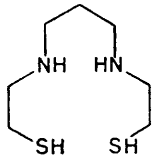

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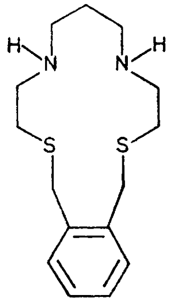

(L^4)

EXPERIMENTAL

Materials.—2-Bromoethylamine hydrobromide was prepared as described by Cortese,[10] yield 71%, m.p. 173—174 °C (lit.,[10] 174—175 °C). Triphenylmethanol was obtained from B.D.H. Triphenylmethanethiol was prepared in almost quantitative yield by the reaction of H_2S with triphenylmethanol in glacial acetic acid.[11] The thiol was recrystallised from methanol. 2-(Triphenylmethylthio)ethylamine (2-tritylthioethylamine, $Ph_3CSCH_2CH_2NH_2$) was prepared in 73% yield by allowing the sodium salt of triphenylmethanethiol to react with 2-bromoethylamine in ethanol,[12] m.p. 88—89 °C (lit.,[12] 90 °C). 1,9-Bis(tritylthio)-3,7-diazanonane dihydrobromide (L$^1\cdot$2HBr) was prepared by heating 2-(triphenylmethylthio)ethylamine (2 mol) with 1,3-dibromopropane (1 mol) in dry toluene solution. The dihydrobromide salt crystallised in 76% yield, m.p. 193—195 °C (decomp.) (Found: C, 64.2; H, 5.9; Br, 18.4. $C_{45}H_{48}Br_2N_2S_2$ requires C, 64.3; H, 5.75; Br, 19.2%).

2-(Benzylthio)ethylamine was prepared by two methods which gave similar yields.

(*a*) 2-Aminoethanethiol hydrochloride was prepared in 87% yield by hydrolysis of thiazoline-2-thione (Aldrich) with concentrated hydrochloric acid under reflux,[13] m.p. 67—70 °C (lit.,[13] 70 °C). To a solution of sodium (23.4 g,

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[1] M. A. Ali and S. E. Livingstone, *Co-ordination Chem. Rev.*, 1974, **13**, 101.

[2] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, 1966, **19**, 1391.

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[4] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, 1967, **6**, 652.

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[6] T. N. Lockyer, *Austral. J. Chem.*, 1974, **27**, 259.

[7] D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Amer. Chem. Soc.*, 1964, **68**, 3642.

[8] M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, 1964, **86**, 3651.

[9] E. Felder and S. Bianchi, *Ann. Chim.* (*Italy*), 1960, **50**, 690.

[10] F. Cortese, *Org. Synth.*, Coll. Vol. 2, 91; *J. Amer. Chem. Soc.*, 1936, **58**, 191.

[11] M. P. Balfe, J. Kenyon, and C. E. Searle, *J. Chem. Soc.*, 1950, 3309.

[12] F. J. Carroll, H. M. Dickson, and M. E. Wall, *J. Org. Chem.*, 1965, **30**, 33.

[13] R. J. Gaul and W. J. Fremuth, *J. Org. Chem.*, 1960, **25**, 869.

1.0 g-atom) in absolute ethanol (900 cm^3) was added 2-aminoethanethiol hydrochloride (56.7 g, 0.50 mol). The mixture was stirred and heated under reflux under nitrogen. A solution of benzyl chloride (63.3 g, 0.50 mol) and sodium iodide (74.9 g, 0.50 mol) in absolute ethanol (350 cm^3) was added dropwise to the gently refluxing mixture. When the addition was complete (*ca.* 1 h) the mixture was stirred and heated under reflux for 14 h under nitrogen. The solution was allowed to cool, the precipitated inorganic salts removed by filtration, and the filtrate evaporated to a small volume. Water (150 cm^3) was added and the amine was extracted with diethyl ether. The ether extracts (5 × 150 cm^3), were combined, washed with water, and dried over Ca[SO$_4$]. The ether was removed *in vacuo* and the residual amine vacuum distilled, b.p. 130—135 °C at 4 mmHg, yield 63.6 g (74.5%).*

(*b*) Phenylmethanethiol [14] was treated with 2-bromoethylamine hydrobromide in the presence of sodium ethoxide as described by Baddiley and Thain,[15] yield 76%.

The amine obtained by the above two methods was a colourless oil which rapidly absorbed CO$_2$ from the atmosphere. The compound was stored over potassium hydroxide pellets in a desiccator. The amine hydrobromide was prepared by treating an ether solution of the amine with hydrogen bromide gas. The oil initially obtained was dissolved in hot propan-2-ol and the solution filtered and cooled. The solid hydrobromide salt was removed by filtration and recrystallised from propan-2-ol, m.p. 130 °C [Found: Br, 32.2 (Volhard). $C_9H_{14}BrNS$ requires Br, 32.3%]. The spectral data for the free amine were as follows: n.m.r. spectrum (in CDCl$_3$) δ 1.27 (2 H, singlet, NH_2), 2.60 (4 H, A_2B_2), 3.63 (2 H, singlet, PhCH_2), and 7.23 p.p.m. (5 H, singlet, aromatics); ν(NH) at 3 365, 3 275, and 3 170, δ(NH$_2$) at 1 585 cm^{-1}.

1,9-Bis(benzylthio)-3,7-diazanonane (L^2) was prepared as follows. 2-(Benzylthio)ethylamine (10 g, 0.06 mol) was dissolved in dry toluene (50 cm^3) and the solution heated under reflux. 1,3-Dibromopropane (6.0 g, 0.03 mol) was added dropwise and the mixture heated under reflux for 4 h and allowed to stand overnight. The precipitated dihydrobromide salt was removed by filtration, washed with diethyl ether, and recrystallised from water containing a little concentrated HBr, m.p. 238 °C (decomp.) (Found: C, 47.1; H, 5.8; Br(ionic), 29.7; N, 5.3. $C_{21}H_{32}Br_2N_2S_2$ requires C, 47.0; H, 6.0; Br, 29.8; N, 5.2%). The free amine was prepared by dissolving the dihydrobromide salt in water, adding excess of sodium hydroxide solution (pH *ca.* 12), extracting with diethyl ether, and removing the ether on a rotatory evaporator.

Metal Complexes.—[1,9-*Bis*(*tritylthio*)-3,7-*diazanonane*]-*cobalt*(II) *bromide*, [CoL^1]Br$_2$. Cobalt(II) acetate tetrahydrate (0.3 g) was heated under reflux with L^1·2HBr (1.0 g) in methanol (50 cm^3) for 2 h under a nitrogen atmosphere. The solution was allowed to stand in a stoppered flask for *ca.* 2 d. The resulting bright blue *product* was filtered off, washed with cold methanol then diethyl ether, and dried *in vacuo* (0.9 g, 70%). The complex is insoluble in water and methanol, but moderately soluble in acetonitrile and chloroform (Found: C, 60.4; H, 5.35; Co, 6.7; N, 3.0. $C_{45}H_{46}Br_2CoN_2S_2$ requires C, 60.2; H, 5.2; Co, 6.6; N, 3.1%).

[1,9-*Bis*(*benzylthio*)-3,7-*diazanonane*]*dibromocobalt*(II), [CoBr$_2$(L^2)]. As for the previous preparation, cobalt(II) acetate tetrahydrate (0.2 g) and L^2·2HBr (0.5 g) were used in methanol (40 cm^3). After 5-h reflux, the solution was cooled and the purple product filtered off, washed with cold methanol and diethyl ether, and dried *in vacuo* (0.46 g, 85%) (Found: C, 42.3; H, 5.2; Co, 9.8; N, 4.7. $C_{21}H_{30}Br_2CoN_2S_2$ requires C, 42.5; H, 5.1; Co, 9.9; N, 4.7%).

[1,9-*Bis*(*benzylthio*)-3,7-*diazanonane*]*dibromonickel*(II), [NiBr$_2$(L^2)]. Nickel(II) acetate tetrahydrate (0.2 g) and L^2·2HBr (0.5 g) were heated under reflux in methanol (40 cm^3). The solution rapidly became blue (no further change was observed on refluxing for *ca.* 10 h). On cooling the blue solution, the *product* crystallised. The complex was removed by filtration, washed with cold methanol then diethyl ether, and dried *in vacuo* (0.43 g, 80%) (Found: C, 42.7; H, 5.15; N, 4.7; Ni, 9.7. $C_{21}H_{30}Br_2N_2NiS_2$ requires C, 42.5; H, 5.1; N, 4.7; Ni, 9.9%).

Bis(3,7-*diazanonane*-1,9-*dithiolato*)*trinickel*(II) *bromide*, [Ni(NiL)$_2$]Br$_2$. Nickel(II) acetate tetrahydrate (0.3 g) and L^1·2HBr (1.0 g) were heated under reflux in methanol (50 cm^3) for 2 h. The solution rapidly turned dark brown and black crystals began to appear. The solution was allowed to stand at room temperature for 1 d. The *product* was filtered off, washed with ice-cold methanol then diethyl ether, and dried *in vacuo* (0.4 g, 55%). The complex is moderately soluble in methanol, but insoluble in water and most other common organic solvents (Found: C, 23.1; H, 4.6; N, 7.5; Ni, 24.6. $C_{14}H_{32}Br_2N_4Ni_3S_4$ requires C, 23.3; H, 4.5; N, 7.8; Ni, 24.4%).

Bis(3,7-*diazanonane*-1,9-*dithiolato*)*trimercury*(II) *bromide trihydrate*, [Hg(HgL)$_2$]Br$_2$·3H$_2$O. To a solution of L^1·2HBr (1.0 g) in hot methanol was added a solution of mercury(II) acetate (0.38 g) in methanol. A white precipitate formed immediately and the resulting suspension was heated under reflux for 2 h, then cooled in an ice-bath. The complex was filtered off, washed with cold methanol then diethyl ether, and dried *in vacuo* (0.9 g, 80%) (Found: C, 13.8; H, 3.0; Hg, 50.3; N, 4.3. $C_{14}H_{38}Br_2Hg_3N_4O_3S_4$ requires C, 14.0; H, 3.2; Hg, 50.1; N, 4.6%). The complex can also be prepared by replacing L^1·2HBr in the above by L^2·2HBr. The trimeric complex is not appreciably soluble in any common solvents.

3,7-*Diazanonane*-1,9-*dithiol Dihydrochloride*.—The complex [Hg(HgL)$_2$]Br$_2$·3H$_2$O was dissolved in the minimum volume of hot 0.1 mol dm^{-3} HCl. Gaseous H$_2$S was passed through the solution and the precipitated mercury(II) sulphide was removed by filtration. The treatment with H$_2$S was repeated, and the resulting filtrate evaporated to dryness on a steam-bath. The residue was recrystallised from methanol containing two drops of concentrated HCl, m.p. 247—249 °C (Found: C, 31.6; H, 7.5; N, 10.6; S, 23.9. $C_7H_{20}Cl_2N_2S_2$ requires C, 31.45; H, 7.5; N, 10.5; S, 24.0%).

Reaction of α,α'-*Dibromo*-o-*xylene with Bis*(3,7-*diazanonane*-1,9-*dithiolato*)*trinickel*(II) *Bromide*.—The nickel(II) trimer (0.5 g) was dissolved in warm methanol and an excess of solid α,α'-dibromo-*o*-xylene (**CAUTION**: lachrymator) was added. The solution was heated on a water-bath for *ca.* 0.5 h. During this time the solution became colourless and blue crystals of the macrocyclic complex were deposited. The crystals were removed by filtration and washed with hot methanol (Found: C, 34.7; H, 4.8; N, 5.4; S, 12.3. $C_{15}H_{24}Br_2N_2NiS_2$ requires C, 35.0; H, 4.7; N, 5.4; S, 12.45%).

Infrared spectra were determined on discs (KBr) using a

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* 1 mmHg ≈ 13.6 × 9.8 Pa; 1 G = 10^{-4} T.

[14] A. I. Vogel, 'Practical Organic Chemistry,' 2nd edn., p. 841.

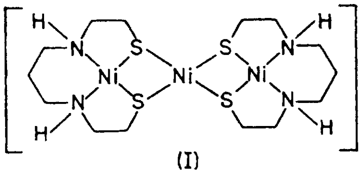
[15] J. Baddiley and E. M. Thain, *J. Chem. Soc.*, 1952, 800.

Perkin-Elmer 457 instrument. Electronic spectra were recorded on a Perkin-Elmer 402 instrument with either spectroscopic grade methanol or chloroform as solvent. Conductivity measurements were made on 10^{-3} mol dm^{-3} solutions of the complexes in methanol using a Portland conductivity meter. Magnetic susceptibilities were measured by the Faraday method using a 6-in Varian electromagnet at a field strength of 16 000 G and a Cahn electrobalance. The equipment was calibrated with $Hg[Co(NCS)_4]$ [16] and $[Ni(en)_3][S_2O_3]$.[17]

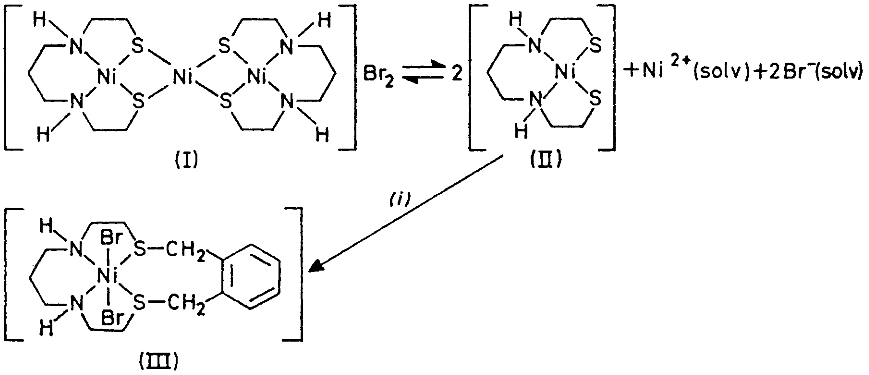
RESULTS AND DISCUSSION

The ligands (L^1) and (L^2) were readily prepared as their dihydrobromide salts by reacting 2-tritylthioethylamine and 2-benzylthioethylamine with 1,3-dibromopropane in toluene solution.

Cobalt(II) acetate reacted with L^2·2HBr in methanol solution to give the purple complex $[CoBr_2(L^2)]$ which has $\lambda_{max.}$ 535 nm (ε 27 dm^3 mol^{-1} cm^{-1}) in chloroform solution. The position and intensity of the band are consistent with an octahedral geometry for this complex.[18] Reaction of cobalt(II) acetate with L^1·2HBr in methanol gave a blue complex with $\lambda_{max.}$ 625 nm (ε 338 dm^3 mol^{-1} cm^{-1}) in chloroform, characteristic of a tetrahedral stereochemistry.[19] Conductivity measurements in methanol confirm that $[CoBr_2(L^2)]$ is a non-electrolyte and $[CoL^1]Br_2$ is a 1 : 2 electrolyte (Λ 150 S cm^2 mol^{-1} at 25 °C). Ligand L^2 has typical aromatic bands at 705s and 770s cm^{-1} in the i.r. spectrum, while L^1 has bands at 705s, 745s, and 755m cm^{-1} (determined for the HBr salts). These bands are retained in the complexes confirming that (in accord with the analytical data) dealkylation does not occur with Co^{II}.



(I)



SCHEME (*i*), $C_6H_4(CH_2Br\text{-}o)_2$

The reaction of nickel(II) acetate with L^2·2HBr in methanol gave a blue octahedral complex having $\lambda_{max.}$ 640 nm (ε 18 dm^3 mol^{-1} cm^{-1}) in chloroform solution which may be assigned to the transition ${}^3T_{1g}\leftarrow{}^3A_{2g}$ (ν_2) in an octahedral ligand field. This complex did not undergo debenzylation even on prolonged heating in methanol solution. The reaction of nickel(II) acetate with L^1·2HBr in methanol solution led to rapid detritylation and the formation of the black diamagnetic complex $[Ni(NiL)_2]Br_2$, (I), containing square-planar nickel. The spectral data are listed in the Table. The trimeric complex lacks any aromatic absorption in the i.r., confirming that complete detritylation has occurred. The complex is a 2 : 1 electrolyte in methanol (Λ 162 S cm^2 mol^{-1} at 25 °C) and is diamagnetic, so that spin pairing of all three nickel atoms occurs. Such sulphur-bridged complexes are well characterised with ligands such as 2-aminoethanethiol [20] and cysteine ethyl ester.[21] The trimeric complex is moderately soluble in methanol, but insoluble in other common solvents. On heating the trimer in methanol with α,α'-dibromo-*o*-xylene the pale blue macrocyclic complex (III) rapidly crystallises from the solution. The thiolate ion when co-ordinated to Ni^{II} remains a powerful nucleophile, and it appears probable that a trimer $\rightleftharpoons$ monomer equilibrium of the type shown in the Scheme is set up, the monomeric complex (II) reacting to give the dibromide. Blinn and Busch [22] studied the kinetics of the reaction of benzyl

Electronic spectra of the complexes

Complex	λ/nm(ε/dm^3 mol^{-1} cm^{-1})
$[CoBr_2(L^2)]$ [a]	535 (27), 324 (680), 260 (sh) (2 220), 245 (2 940)
$[CoL^1]Br_2$ [a]	625 (338), 260 (sh) (4 460), 242 (6 320)
$[NiBr_2(L^2)]$	640 (18), 390 (30), 269 (4 470), 244 (sh) (3 770)
$[Ni(NiL)_2]Br_2$ [b]	558 (1 800), 485 (2 440), 410 (5 600), 306 (17 600), 281 (sh) (11 660), 265 (sh) (14 600), 242 (sh) (21 000), 213 (28 700)

[a] In $CHCl_3$ [b] In methanol.

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[16] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.

[17] N. F. Curtis, *J. Chem. Soc.*, 1961, 3147.

[18] M. Keeton, A. B. P. Lever, and B. S. Ramaswamy, *Canad. J. Chem.*, 1970, **48**, 3185.

[19] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968, p. 333.

[20] (*a*) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, 1962, **1**, 872; (*b*) see D. H. Busch in 'Reactions of Coordinated Ligands and Homogeneous Catalysis,' *Adv. Chem. Ser.*, No. 37, Amer. Chem. Soc., Washington, 1963.

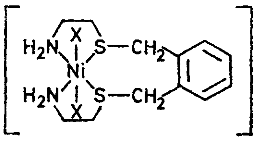
[21] L. J. Porter, D. D. Perrin, and R. W. Hay, *J. Chem. Soc.* (*A*), 1969, 118.

[22] E. L. Blinn and D. H. Busch, *J. Amer. Chem. Soc.*, 1968, **90**, 4280.

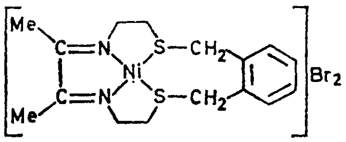
bromide with a variety of thioaminenickel(II) complexes. The kinetics are consistent with pre-equilibrium co-ordination of the halide to the nickel(II) ion, followed by rate-determining nucleophilic substitution by the co-ordinated sulphur. Co-ordination by the metal ion is presumed to promote breaking of the C–Br bond.

The macrocyclic complex (III) is blue in colour, paramagnetic, and is insoluble in the common solvents. The solid-state reflectance spectrum has three bands at 10 600, 17 000, and 27 000 cm^{-1} which may be assigned to the transitions $^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1), $^3T_{1g} \leftarrow {}^3A_{2g}$ (ν_2), and $^3T_{1g}$ $(P) \leftarrow {}^3A_{2g}$ (ν_3) in an octahedral ligand field. The ratio of the frequencies $\nu_2 : \nu_1$ is 1.60 : 1 which is within the range 1.5—1.7 : 1 expected for octahedral stereochemistry about the central nickel atom.[23]

Complexes of type (IV), first described by Thompson and Busch,[24] are blue and paramagnetic indicating six-co-ordinate nickel. The ring-closed complexes (V)[24] are brown and diamagnetic, becoming paramagnetic in aqueous solution, presumably due to formation of octahedral diaqua-species. The introduction of the di-imine linkages into the macrocycle (V) is sufficient to bring about spin pairing due to the increased ligand field of the unsaturated macrocycle. The macrocyclic complexes of the type (III) which are essentially saturated are thus more comparable to the non-cyclic complexes (IV) in their ligand-field strength.



(IV) X = Cl or Br



(V)

Mercury(II) acetate reacts with both L^1 and L^2 in methanol solution to give the trinuclear complex [Hg(HgL)$_2$]Br$_2$·3H$_2$O. Complete dealkylation is confirmed by the i.r. spectrum of the product which lacked any bands attributable to aromatic groups. Although trinuclear mercury complexes of this type do not appear to have been previously reported, trinuclear cadmium(II) and mercury(II) complexes of the types [Hg{Ni(NH$_2$CH$_2$CH$_2$S)$_2$}$_2$][HgCl$_4$] and [Cd{Ni(NH$_2$CH$_2$CH$_2$S)$_2$}$_2$][CdCl$_4$] are known.[23] The mercury(II) trimer can be decomposed by 0.1M hydrochloric acid and the mercury(II) precipitated by hydrogen sulphide. Concentration of the filtered solution gives the dihydrobromide salt of 3,7-diazanonane-1,9-thiol. Previous methods[9] for the preparation of this ligand have used a rather low-yield sodium–liquid-ammonia reduction of 1,9-bis(benzylthio)-3,7-diazanonane. The present route provides a more satisfactory synthesis of the ligand.

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[23] E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev.*, 1968, **22**, 457.

[24] M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, 1964, **86**, 3651.