Some Transition-metal Complexes derived from the Ligand $[Ph_3CS(CH_2)_2NHCH_2]_2CH_2$ † and the Crystal Structure of $[Pd\{\overline{S(CH_2)_2NH(CH_2)_3NH(CH\ )_2SNi}\}_2]^{2+}$ ‡

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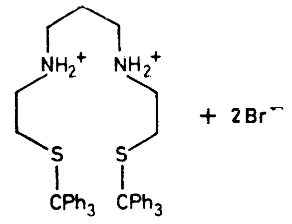
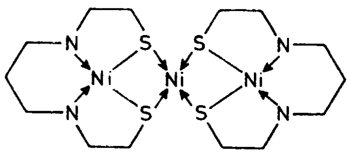
S-Dealkylation of the ligand $[Ph_3CS(CH_2)_2NHCH_2]_2CH_2$ occurs when it is treated with certain bivalent metal ions (Ni^{2+}, Cd^{2+}, or Pd^{2+}). The products are trimeric species of general form $[M\{\overline{S(CH_2)_2NH(CH_2)_3NH(CH_2)_2SM}\}_2]^{2+}$ (M = metal). By allowing the nickel trimer to react with Pd^{2+} or Cd^{2+}, mixed-metal trimers were obtained of formula $[M\{\overline{S(CH_2)_2NH(CH_2)_3NH(CH_2)_2SNi}\}_2]^{2+}$ (M = Pd or Cd). The crystal structure of one such salt with M = Pd is reported. The associated anion consists of 38.5% Br^- and 61.5% NCS^-. The crystals are monoclinic, space group $P2_1/c$, with $Z = 2$, $a = 7.957(8)$, $b = 15.127(10)$, $c = 10.988(11)$ Å, and $\beta = 105.2(1)°$. A total of 747 reflections above background have been refined to R 0.070. The cation has crystallographically imposed $\bar{1}$ symmetry with the palladium atom in a planar S_4 environment [Pd–S 2.338(9), 2.337(9) Å]. The nickel atoms also have planar environments [Ni–S 2.182(11), 2.181(10); Ni–N 1.97(2), 1.96(2) Å] with the PdS_4 and NiS_2N_2 planes intersecting at an angle of 121°.

SULPHUR atoms in ligands exhibit a wide range of bonding modes with a great propensity to acting as a bridge between two or more metal atoms.[1,2] Two other interesting features of sulphur co-ordination chemistry are the *S*-dealkylation reactions, observed when thioethers co-ordinate to a metal,[1-6] and the reverse process, alkylation of a co-ordinated mercapto-group.[3,7-10] In studying the chemistry of the ligand $Ph_3CS(CH_2)_2NH(CH_2)_3NH(CH_2)_2SCPh_3{\cdot}2HBr$ ($L^1{\cdot}2HBr$) it has been shown that this ligand, together with compounds derived from it, exhibit all three features of sulphur co-ordination chemistry outlined above.[11] For example $Ph_3CS(CH_2)_2NH(CH_2)_3NH(CH_2)_2SCPh_3$ (L^1) when treated with nickel(II) acetate undergoes an *S*-dealkylation reaction with the formation of the trimeric species $[Ni(NiL^2)_2]^{2+}$ $\{L^2 = [^-S(CH_2)_2NHCH_2]_2CH_2$, 3,7-diazanonane-1,9-dithiolate$\}$ in which the RS^- species link two metal centres. The *S*-dealkylation reaction depends upon the nature of the metal ion [with cobalt(II), L^1 gives a simple co-ordination compound] and the nature of the leaving group [on changing the CPh_3 groups in L^1 to CH_2Ph groups the resulting ligand does not undergo *S*-dealkylation on reaction with nickel(II) but instead forms a simple adduct]. Finally it was shown that the reaction of $[Ni(NiL^2)_2]^{2+}$ with an alkyl halide resulted in an alkylation reaction.[11]



$L^1{\cdot}2HBr$



$[Ni(NiL^2)_2]^{2+}$

We have extended the previously reported work on L^1.[11] In particular, we have prepared a range of mixed-metal trimeric clusters and determined, by single-crystal *X*-ray techniques, the structure of $[Pd(NiL^2)_2]^{2+}$. Our interest in these mixed-metal complexes arose from our desire to establish whether reaction (1) (M = metal

$$[Ni(NiL^2)_2]^{2+} \rightleftharpoons 2NiL^2 + Ni^{2+} \xrightleftharpoons{M^{2+}} [M(NiL^2)_2]^{2+} \quad (1)$$

atom) took place, for while nickel(II) monomeric complexes of $NH_2CH_2CH_2S^-$, *i.e.* $[Ni(SCH_2CH_2NH_2)_2]$, as well as trinuclear species $[Ni\{(SCH_2CH_2NH_2)_2Ni\}_2]^{2+}$ have been reported, no evidence for the mononuclear NiL^2 has been presented.

EXPERIMENTAL

Preparation of $Ph_3CSCH_2CH_2NH_2$.—While being heated under reflux, an ethanolic solution of 2-bromoethylamine hydrobromide and sodium was allowed to react with Ph_3CSH (molar ratio 1 : 2 : 1) under an atmosphere of N_2 for 12 h. The nature of the product, $Ph_3CSCH_2CH_2NH_2$, was determined by elemental analyses (C, H, and N) and n.m.r. spectroscopy. The product was stored in an atmosphere of dry N_2 over K[OH] pellets.

Preparation of $Ph_3CS(CH_2)_2NH(CH_2)_3NH(CH_2)_2SCPh_3$ (L^1).—To a boiling solution of $Ph_3CSCH_2CH_2NH_2$ (0.1 mol) dissolved in sodium-dried toluene was added dropwise (over 0.5 h) 1,3-dibromopropane (0.05 mol). The heating was continued for a further 4 h and the resulting mixture allowed to cool overnight during which time the dihydrobromide salt $\{Ph_3CS(CH_2)_2NHCH_2\}_2CH_2{\cdot}2HBr$ precipitated. The salt was filtered off and recrystallised from ethanol containing a little HBr. The nature of the product was determined by elemental analyses (C, H, N, and Br) and n.m.r. spectroscopy.

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† 1,9-Bis(tritylthio)-3,7-diazanonane.

‡ Bis[(3,7-diazanonane-1,9-dithiolato-*NN′SS′*-nickel)-*SS′*]-palladium(II).

Compounds derived from L^1.—(*a*) *Preparation of* $[Ni(NiL^2)_2]X_2$ (X = NCS, Cl, I, Br, *or* ClO_4).[11] Nickel(II) acetate tetrahydrate (0.3 g) in methanol (20 cm³) was added to a solution of $L^1\cdot 2HBr$ (1.0 g) in methanol (30 cm³) and heated under reflux for 2 h. On cooling, a black crystalline material formed which was filtered off, washed with cold methanol and diethyl ether, and finally dried *in vacuo* over P_2O_5. The yield was 55% (for X = Br).

Anion-exchange reactions were carried out by treating methanolic solutions of salts (*e.g.* Li[NCS] and $Na[ClO_4]$) with the bromide of the nickel trimer.

(*b*) *Preparation of* $[Cd(CdL^2)_2]Br_2$. The cadmium salt was prepared by the same method as the nickel(II) complex (see above) using cadmium acetate.

(*c*) *Preparation of* $[Pd(PdL^2)_2][PdBr_4]$. Palladium(II) acetate (0.8 g) in methanol (20 cm³) was added dropwise to a methanolic solution (50 cm³) of $L^1\cdot 2HBr$. The mixture was maintained at 40 °C overnight. If the solution was allowed to reflux palladium black was formed.

The product which formed as an orange crystalline mass on cooling of the methanolic solution was filtered off, washed with diethyl ether, and stored over P_2O_5.

Attempts to carry out the preparation with PdX_4^{2-} anions (X = Cl or Br) were unsuccessful.

(*d*) *Preparation of mixed-metal complexes.* (i) $[M(NiL^2)_2]Br_2$. To a methanolic solution (30 cm³) of $[Ni(NiL^2)_2]Br_2$ (0.4 g) was added a methanolic solution (20 cm³) of either palladium(II) or cobalt(II) acetate (molar ratio of reactants 2 : 1). The mixture was maintained at 40 °C (M = Pd) for 3 h or heated under reflux for 4 h (M = Co). The mixture was allowed to cool overnight and the precipitated product (M = Pd: rust-red, M = Co: black) was filtered off, washed with diethyl ether, and dried over P_2O_5.

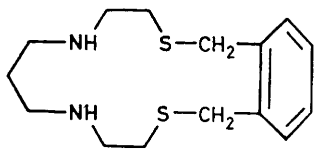
(ii) $[Pd(NiL^2)_2][NCS]_2$ *and* $[Pd(NiL^2)_2][Pd(NCS)_4]$. The thiocyanate $[Pd(NiL^2)_2][NCS]_2$ was prepared by anion exchange from the appropriate bromide, using a methanolic solution of Li[NCS]. Occasionally it was difficult to ensure complete anion exchange as shown by the single-crystal study reported here. The bromide anion was also replaced by $[Pd(NCS)_4]^{2-}$ by treating a methanolic solution of the bromide salt with palladium(II) acetate (1 : 1 molar ratio) in the presence of a large excess of Li[NCS].

(iii) $[Cd(NiL^2)_2][CdBr_4]$. Equimolar amounts of cadmium acetate and $[Ni(NiL^2)_2]Br_2$ (1 mmol) were gently heated in methanol. To the mixture was added a small volume of concentrated HBr (0.5 cm³). The mixture was heated for 1 h and allowed to cool overnight. The product which was isolated as a dark red solid was washed with diethyl ether and stored over P_2O_5.

(iv) $[Pt(NiL^2)_2][PtBr_4]$. Sodium bromoplatinate(II) (0.8 g) and $[Ni(NiL^2)_2]Br_2$ (0.4 g) were dissolved in methanol (60 cm³) and the mixture heated under reflux for 4 h. An orange product separated from the cooled solution. The precipitate was filtered off, washed well with methanol and diethyl ether, and dried over P_2O_5.

Preparation of Complexes of L^4.—To $[Ni(NiL^2)_2]Br_2$ (0.13 g) dissolved in methanol (30 cm³) and being heated under reflux, was added a small excess of α,α′-dibromo-*o*-xylene (0.5 g). Heating was continued for a further 2.5 h. During this time the solution which had been dark brown became blue and the product precipitated. The blue complex was filtered off, washed well with methanol and diethyl ether, and dried over P_2O_5.

Iodide, thiocyanate, and bromoperchlorate derivatives were prepared from the bromide by metathesis with a methanolic solution of an appropriate reagent (KI, Li[NCS], or $Na[ClO_4]$). Attempts to prepare the chloride failed; the product always being mixed with bromide {Found: C, 34.7; H, 5.0; N, 5.0; Ni, 11.1. $[NiBrL^4]Br$ requires C, 35.0; H, 4.7; N, 5.4; Ni, 11.4%. Found: C, 28.9; H, 3.6; N, 4.9; Ni, 9.9. $[NiIL^4]I$ requires C, 29.6; H, 3.9; N, 4.6; Ni, 9.6%. Found: C, 33.3; H, 4.8; N, 5.0; Ni, 10.9. $[NiBr(ClO_4)L^4]$ requires C, 33.7; H, 4.5; N, 5.2; Ni, 11.0%. Found: C, 41.7; H, 4.5; N, 11.2; Ni, 12.0. $[Ni(NCS)_2L^4]$ requires C, 43.0; H, 5.1; N, 11.8; Ni, 12.5%}.



L^4

Physical Measurements—Infrared spectra (Nujol mulls) were determined using a Perkin-Elmer 577 instrument. Electronic spectra were measured on a Beckmann Acta Mk. (IV) spectrometer that was fitted with a reflectance sphere for measurements on solid samples. Magnetic measurements were carried out using Newport Instruments equipment, both the Gouy (variable temperature) and Faraday (room temperature) methods being employed.

X-*Ray Crystallographic Measurements.*—Crystals of $Ni_2Pd(C_7H_{16}N_2S_2)_2Br_{0.77}(NCS)_{1.23}$ were obtained during an attempted ion exchange of thiocyanate for bromide, using a methanolic solution of Li[NCS]. We could not prepare crystals of the pure bromide or pure thiocyanate.

Crystal data. $C_{15.23}H_{32}Br_{0.77}N_{5.23}Ni_2PdS_{5.23}$, $M = 741.3$, Monoclinic, $a = 7.957(8)$, $b = 15.127(10)$, $c = 10.988(11)$ Å, $\beta = 105.2(1)°$, $U = 1\,269.2$ Å³, $D_c = 1.94$, $D_m = 1.87$ g cm⁻³, $Z = 2$, $F(000) = 758.6$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 38.6$ cm⁻¹, space group $P2_1/c$ from systematic absences $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$.

A crystal with dimensions 0.20 × 0.35 × 0.60 mm was mounted with the (100) planes perpendicular to the instrument axis of a General Electric X.R.D. 5 which was used to measure diffraction intensities and cell dimensions. The instrument was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. The stationary-crystal-stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections monitored during the course of the experiment showed no significant changes in intensity. A total of 1 310 independent reflections were measured for $2\theta < 40°$. No absorption or extinction corrections were applied. The standard deviations $\sigma(I)$ of the reflections were taken to be $[I + 2E + (0.03I)^2]^{\frac{1}{2}}$, where I is the intensity and E is the estimated background of the reflection. 747 Reflections with $I > 3\sigma(I)$ were used in the subsequent refinement. Neither an absorption nor an extinction correction was made.

Structure Determination.—The positions of the Pd and Ni atoms were determined from a Patterson function and Fourier syntheses were used to determine the positions of the remaining atoms in the cation.

The electron-density map for the anion was difficult to interpret. However, when we realised that the anion exchange had not proceeded to completion and that the asymmetric unit contained both Br^- and NCS^- anions with a combined occupancy of 1.0, a suitable treatment for this disorder suggested itself. The bromide ion was given an occupancy factor of x and the thiocyanate $1 - x$, x being refinable. The geometry of the thiocyanate ion was originally fixed with C–N, C–S, N · · · S at 1.20(5), 1.58(5), and 2.70(5) Å respectively but in the final cycles of least squares, atomic co-ordinates for the NCS^- anion were refined independently. The bromide ion was given anisotropic thermal parameters and the thiocyanate isotropic thermal parameters. These all refined to reasonable values, as did x to 0.38(2). A difference-Fourier map in this region showed the electron density had been satisfactorily explained.

TABLE 1

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	X	Y	Z
Pd	0(0)	0(0)	0(0)
Ni	−2 758(5)	449(3)	1 232(4)
S(1)	−1 964(11)	1 177(6)	−239(8)
C(2)	−1 058(41)	2 156(23)	689(31)
C(3)	−2 404(39)	2 349(21)	1 495(30)
N(4)	−2 706(29)	1 546(15)	2 200(21)
C(5)	−4 131(43)	1 683(23)	2 790(31)
C(6)	−4 173(42)	940(21)	3 752(30)
C(7)	−4 384(46)	−14(25)	3 202(34)
N(8)	−3 082(30)	−261(15)	2 646(21)
C(9)	−3 146(46)	−1 214(24)	2 330(32)
C(10)	−2 087(52)	−1 479(28)	1 552(36)
S(11)	−2 494(11)	−745(6)	185(8)
Br(1)	1 121(19)	925(13)	4 047(16)
N(12)	1 199(83)	−289(51)	3 217(60)
C(13)	1 214(91)	498(67)	3 475(74)
S(14)	1 249(43)	1 226(19)	4 311(30)

In the final refinement the Pd, Ni, and S atoms were also given anisotropic thermal parameters, while the nitrogen and carbon atoms were refined isotropically. Hydrogen atoms were introduced in fixed tetrahedral positions but their parameters were not refined.

TABLE 2

Bond lengths (Å) and angles (°)

Pd · · · Ni	2.944(5)	N(4)–C(5)	1.46(5)
Pd–S(1)	2.338(9)	C(5)–C(6)	1.55(5)
Pd–S(11)	2.337(9)	C(6)–C(7)	1.56(5)
Ni–S(1)	2.182(11)	C(7)–N(8)	1.39(5)
Ni–N(4)	1.97(2)	N(8)–C(9)	1.48(4)
Ni–N(8)	1.96(2)	C(9)–C(10)	1.41(6)
Ni–S(11)	2.181(10)	C(10)–S(11)	1.83(4)
S(1)–C(2)	1.83(3)	N(12)–C(13)	1.2(1)
C(2)–C(3)	1.59(5)	C(13)–S(14)	1.4(1)
C(3)–N(4)	1.49(4)		

S(1)–Pd–S(11)	79.6(3)	Ni–N(4)–C(3)	112.9(19)
S(1)–Pd–S(11$^{\text{I}}$) *	100.4(3)	Ni–N(4)–C(5)	116.8(19)
S(1)–Ni–N(4)	90.3(8)	N(4)–C(5)–C(6)	111.0(26)
S(1)–Ni–N(8)	170.9(7)	C(5)–C(6)–C(7)	115.3(28)
S(1)–Ni–S(11)	86.6(4)	C(6)–C(7)–N(8)	113.9(29)
N(4)–Ni–N(8)	91.3(10)	C(7)–N(8)–C(9)	112.5(27)
N(4)–Ni–S(11)	173.4(8)	Ni–N(8)–C(9)	110.6(20)
N(8)–Ni–S(11)	90.9(7)	Ni–N(8)–C(7)	118.1(20)
Ni–S(1)–C(2)	98.3(12)	N(8)–C(9)–C(10)	115.5(33)
Ni–S(1)–Pd	81.2(3)	C(9)–C(10)–S(11)	108.7(28)
C(2)–S(1)–Pd	113.5(10)	C(10)–S(11)–Ni	95.2(14)
S(1)–C(2)–C(3)	103.6(21)	Pd–S(11)–Ni	81.3(3)
C(2)–C(3)–N(4)	111.3(25)	C(10)–S(11)–Pd	113.1(13)
C(3)–N(4)–C(5)	111.3(24)	N(12)–C(13)–S(14)	154(8)

* Superscript I refers to the equivalent position $\bar{x}$, $\bar{y}$, $\bar{z}$.

The final R value was 0.070. Calculations were done at the University of London Computer Centre with the Shelx system of programs.[12] Scattering factors were taken from International Tables.[13] The weighting scheme used was chosen to give average values of $w\Delta^2$ for groups of reflections over ranges of $(\sin\theta)/\lambda$ and F; $\sqrt{w} = 1$ for $F_o < 50$ and $50/F_o$ for $F_o > 50$. In the final cycle of refinement all shifts were $< 0.05\sigma$ and none of the unobserved reflections showed any serious discrepancy. Final atomic co-ordinates are given in Table 1. Observed and calculated structure factors, and thermal parameters, are given in Supplementary Publication No. SUP 22847 (7 pp.).* Bond lengths and angles are given in Table 2.

RESULTS AND DISCUSSION

Dealkylation and the formation of species of the type $[M(ML^2)_2]^{2+}$ occurs when $[Ph_3CS(CH_2)_2NHCH_2]_2CH_2\cdot 2HBr$ ($L^1\cdot 2HBr$) is treated with Ni^{2+}, Cd^{2+}, or Pd^{2+}. With cobalt(II) acetate a co-ordination compound is obtained $[CoL^1]Br_2$ while with copper(II) a complex reaction takes place and a diamagnetic purple compound is formed whose analysis, although reproducible, does not agree with any reasonable formulation. The compounds that have been isolated are listed in Table 3.

The compound containing three nickel atoms has been reported previously together with an analogous mercury derivative.[11] It was suggested an equilibrium existed between monomeric and trimeric species [see equation (1)].

To confirm the nature of the equilibrium, the nickel trimer was allowed to react with $PtBr_4^{2-}$, palladium(II), cobalt(II), and cadmium(II) acetates and hence mixed-metal cations whose analyses accord with the formulation $[M(M^1L^2)_2]^{2+}$ were obtained. However, the formulation $[Ni(NiL^2)(ML^2)]^{2+}$ would also fit the analyses; such compounds can be envisaged as being formed *via* a series of equilibria in which ML^2 is first formed.

All the mixed-metal complexes [except that formed with cobalt(II)] were diamagnetic, an observation which does not distinguish between the two proposed structures for the mixed-metal ion. With all the trimeric nickel species the nature of the associated anion was shown to affect the magnetic moment; thus when the anion was Br^-, Cl^-, I^-, or ClO_4^- the compounds were diamagnetic but with the thiocyanate anion the magnetic moment was 1.18 B.M.† per nickel atom.

These observations are evidence for all the nickel compounds (except that of the thiocyanate derivative) having the metal ions in square-planar environments, while the central nickel atom in the thiocyanate derivative is in a D_{4h} environment. The i.r. spectrum of this latter compound suggests that the anions are bonded through the nitrogen atoms, thus, the central metal atom is in a co-ordination sphere composed of four sulphur and two nitrogen atoms. The change in stereochemistry from square-planar, with Cl^-, Br^-, I^-, and ClO_4^-, to octahedral with nitrogen-bonded NCS^- is in accord with the relative positions of these ions in the spectrochemical series and their size.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

† Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

TABLE 3

Analytical data

Complex	Colour	Found (%) C	H	N	Metal	Required (%) C	H	N	Metal
$[\mathrm{Ni(NiL^2)_2}]\mathrm{Br_2}$	Black	23.5	4.3	6.7	24.8	23.3	4.5	7.8	24.5
$[\mathrm{Ni(NiL^2)_2}]\mathrm{Cl_2{\cdot}H_2O}$	Black	25.4	5.3	8.2	26.9	25.8	5.2	8.6	27.1
$[\mathrm{Ni(NiL^2)_2}]\mathrm{I_2}$	Brown-black	20.0	4.3	6.4	21.6	20.6	3.9	6.9	21.6
$[\mathrm{Ni(NiL^2)_2}][\mathrm{ClO_4}]\mathrm{Br}$	Black	22.8	4.5	7.5	23.8	22.7	4.3	7.6	23.8
$[\mathrm{Ni(NCS)_2(NiL^2)_2}]$	Dark brown	24.9	4.4	10.2	26.3	24.9	4.7	12.4	26.0
$[\mathrm{CoL^1}]\mathrm{Br_2}$	Bright blue	60.3	5.4	2.9	6.6	60.2	5.2	3.1	6.6
$[\mathrm{Cd(CdL^2)_2}]\mathrm{Br_2}$	White	18.2	3.4	6.5		19.1	3.6	6.4	38.1
$[\mathrm{Pd(PdL^2)_2}][\mathrm{PdBr_4}]$	Dark orange	14.9	2.9	4.1	37.3	14.8	2.8	4.9	37.7

Complex	Colour	Found (%) C	H	N	Ni	Metal	Required (%) C	H	N	Ni	Metal
$[\mathrm{Co(NiL^2)_2}]\mathrm{Br_2}$	Black	23.8	4.5	7.5		Co, 8.1	23.3	4.4	7.8	16.0	Co, 8.2
$[\mathrm{Pd(NiL^2)_2}]\mathrm{Br_2}$	Rust-red	21.7	4.5	6.9	15.3	Pd, 14.1	21.9	4.2	7.3	15.3	Pd, 13.9
$[\mathrm{Pd(NiL^2)_2}][\mathrm{Pd(NCS)_4}]$	Red	22.9	3.9	11.2	12.6	Pd, 22.0	22.8	3.4	11.8	12.4	22.4
$[\mathrm{Cd(NiL^2)_2}][\mathrm{CdBr_4}]$	Dark red	16.3	3.0	5.1		20.5	16.1	3.1	5.3	11.2	21.5
$[\mathrm{Pt(NiL^2)_2}][\mathrm{PtBr_4}]$	Orange	14.6	3.6	6.0	9.6		13.9	2.6	4.6	9.7	

$\mathrm{L^1 = [Ph_3CS(CH_2)_2NH_2CH_2]_2CH_2}$, $\mathrm{L^2 = [S(CH_2)_2NHCH_2]_2CH_2}$.

The u.v.-visible spectra of $[\mathrm{Ni(NiL^2)_2}]\mathrm{X_2}$ (X = Cl, Br, I, or $\mathrm{ClO_4}$) were all measured by reflectance and solution techniques (in $\mathrm{CH_3OH}$) and there were no changes in the spectra with phase. The results are in accord with those previously published (X = Br) [11] except that in addition to the previously reported bands we have detected three pronounced shoulders [809 nm ($\varepsilon_{\mathrm{max.}} = 24\ \mathrm{m^2\ mol^{-1}}$), 740 nm ($\varepsilon_{\mathrm{max.}} = 41\ \mathrm{m^2\ mol^{-1}}$), and 640 nm ($\varepsilon_{\mathrm{max.}} = 70\ \mathrm{m^2\ mol^{-1}}$)]. The compound containing $\mathrm{NCS^-}$ has a very similar spectrum to the other trimeric nickel compounds below 740 nm but above this wavelength it has an absorption at 1 105 nm. This band we assign to a $^3T_{2g}(F) \leftarrow {}^3A_{2g}$ transition of the central nickel ion, which gives a Dq value of 905 $\mathrm{cm^{-1}}$, not an unreasonable value for a $\mathrm{N_2S_4}$ (NCS) co-ordination sphere.[14]

Reaction of the mixed palladium–nickel bromide trimer with Li[NCS] gave a thiocyanate derivative that could be formulated as either $[\mathrm{Pd(NiL^2)_2}][\mathrm{NCS}]_2$ or $[\mathrm{Ni(NiL^2)(PdL^2)}][\mathrm{NCS}]_2$. Magnetic measurements on the trimeric palladium–nickel thiocyanate showed it to be diamagnetic, thus suggesting, in view of the magnetic moment of the all nickel thiocyanate trimer, the first of the two postulated formulations to be the correct one. To confirm this, attempts were made to grow crystals suitable for *X*-ray structural investigation of a range of trimers. Unfortunately only one batch of crystals containing the $[\mathrm{Pd(NiL_2)_2}]^{2+}$ ion and a random mixture of $\mathrm{Br^-}$ and $\mathrm{NCS^-}$ proved amenable for study.

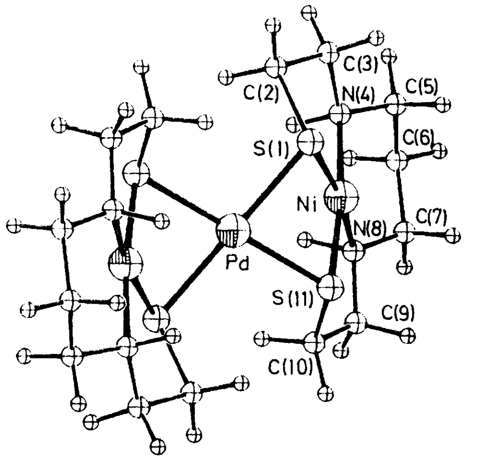


FIGURE 1 The structure of $[\mathrm{Pd\{Ni[S(CH_2)_2NHCH_2]_2CH_2\}_2}]^{2+}$

The Structure of the Complex

$[\mathrm{Pd}\{\overline{\mathrm{S(CH_2)_2NH(CH_2)_3NH(CH_2)_2SNi}}\}_2]^{2+}$.—The unit cell contains two centrosymmetric cations of $[\mathrm{Pd(NiL^2)_2}]^{2+}$ (Figures 1 and 2). The palladium and nickel atoms are in approximately square-planar environments. The palladium atom which is at the centre of symmetry is co-ordinated to four sulphur atoms [bond lengths: 2.338(9) and 2.337(9) Å], the $\mathrm{PdS_4}$ group being perforce

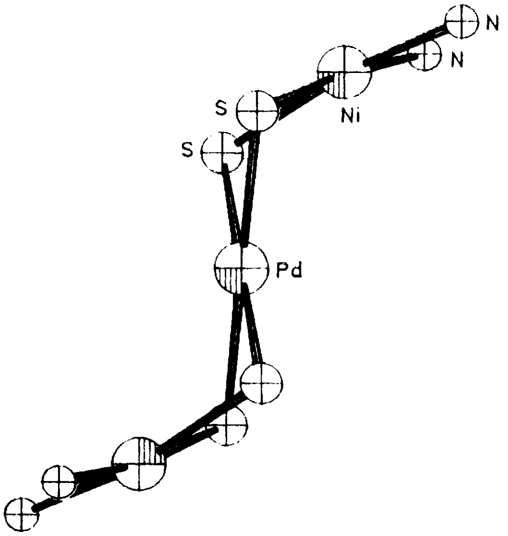


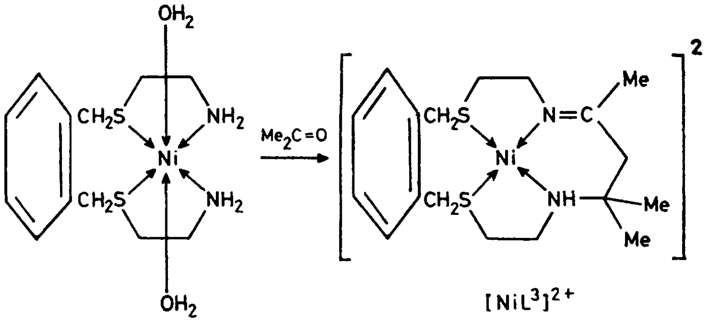
FIGURE 2 The ' chair ' shape of the $\mathrm{N_2NiS_2PdS_2NiN_2}$ fragment in the trimeric cation

planar. However, the angles subtended at the palladium atom are by no means right angles being 79.6(3) [S(1)–Pd–S(11)] and 100.4(3) [S(1)–Pd–S(11^{I})].

Each nickel atom is co-ordinated to two nitrogen and two sulphur atoms from one quadridentate ligand. The Ni–S [2.182(11), 2.181(10) Å] and Ni–N [1.97(2) to N(4), 1.96(2) Å to N(8)] distances are in agreement with the related ones found in $[\mathrm{Ni}\{[\mathrm{S(CH_2)_2NH_2}]_2\mathrm{Ni}\}_2]^{2+}$ [2.212(4) to S and 1.902(3), 1.926(7) Å to N].[15] The environment of the nickel atom is distorted from planarity, being 0.13 Å above S(1), S(11), N(4), and N(8) which are themselves coplanar to within 0.02 Å. Both the structure reported here and that of $[\mathrm{Ni}\{[\mathrm{S(CH_2)_2NH_2}]_2\mathrm{Ni}\}_2]^{2+}$ exist as ' chair ' species (Figure 2) and can be considered as being formed by two mononuclear complexes co-ordinating through two sulphur atoms to a further metal ion. The differences between related distances and angles in the two structures may be attributed to the change in metal radii on going from a central Ni to a central Pd atom and the presence, in the structure reported here, of a $(\mathrm{CH_2})_3$ bridge linking the two nitrogen atoms N(4) and N(8). The presence of the bridge causes the N–Ni–N angle to decrease from 96.1(3) to 91.3(10)° and the S–Ni–S angle to increase from 84.0(2) to 86.6(4), thus leaving the *cis* S–Ni–S angles the same within experimental error.

Exchange of the central Ni atom for Pd brings about a closing of the S–M–S angle (M = central metal atom) from 81.4(2) to 79.6(3)° and the opening of the $\mathrm{M^1}$–S–M angle from 77.5 ($\mathrm{M^1}$ = M = Ni) to 81.2(3)° ($\mathrm{M^1}$ = Ni, M = Pd). The metal–metal distance also changes [Ni–Ni 2.733(7),[15] Ni–Pd 2.944(4) Å], the alteration (0.21 Å) being of the order expected when the difference in the ionic radii (Ni 0.49, Pd 0.64 Å) [16] and the accuracy of these values are considered.

In the nickel trimer $[\mathrm{Ni}\{[\mathrm{S(CH_2)_2NH_2}]_2\mathrm{Ni}\}_2]^{2+}$ the authors consider the Ni · · · Ni distance of 2.733(7) Å to be indicative of a weak metal–metal bond. We are not convinced by their arguments since it seems likely the metals are brought into close proximity by the bridging sulphur atoms. In the present structure it is even less likely that there is a metal–metal interaction as the angle between the $\mathrm{PdS_2}$ and $\mathrm{NiS_2}$ planes is 121° compared to 109° in the nickel trimer.



$[\mathrm{NiL^3}]^{2+}$

(2)

Torsion angles for the ligand (Table 4) and least-squares planes (SUP 22847) show that the ligand conformation is relatively strain free. The two five-membered rings are asymmetrically puckered and the six-membered ring is in the chair form. As well as the two centrosymmetric cations the unit cell contains a bromide ion (38.5%), and the thiocyanate anions (61.5%) in general positions. There are no intermolecular distances less than the sum of the appropriate van der Waals radii and the closest contacts involving an atom in the $\mathrm{Br^-/NCS^-}$ anions are N(4) · · · Br(1) 3.32 and N(8) · · · N(12) 3.30 Å.

TABLE 4

Torsion angles (°)

Ni–S(1)–C(2)–C(3)	−41.2
S(1)–C(2)–C(3)–N(4)	54.8
C(2)–C(3)–N(4)–C(5)	−171.5
C(3)–N(4)–C(5)–C(6)	−167.4
N(4)–C(5)–C(6)–C(7)	−58.6
C(5)–C(6)–C(7)–N(8)	58.6
C(6)–C(7)–N(8)–C(9)	170.2
C(7)–N(8)–C(9)–C(10)	168.3
N(8)–C(9)–C(10)–S(11)	−50.0
C(9)–C(10)–S(11)–Ni	38.2

Macrocyclic Complexes.—Urbach and Busch [17] have reported the synthesis of some nickel(II) complexes containing the ligand $\mathrm{L^3}$ [see equation (2)]. They found that the stereochemistry of the metal ion in the complexes based upon $[\mathrm{NiL^3}]^{2+}$ varied with the anion, thus when the anion was $\mathrm{Cl^-}$, $\mathrm{Br^-}$, or $\mathrm{I^-}$ five-co-ordinate species were detected, with $\mathrm{NCS^-}$ the compound was six-co-ordinate, and with $\mathrm{ClO_4^-}$ a square-planar compound was formed.

By treating α,α'-dibromo-*o*-xylene with $[\mathrm{Ni(NiL^2)_2}]\mathrm{Br_2}$ the compound $[\mathrm{NiBrL^4}]\mathrm{Br}$ was isolated.[11]

We decided to extend the work of Hay *et al.*[11] to ascertain if the stereochemistry of the nickel atom in $\mathrm{L^4}$ complexes is dependent upon the anion as observed with $[\mathrm{NiL^3}]^{2+}$ compounds.[17] Accordingly we prepared the bromide $[\mathrm{NiBrL^4}]\mathrm{Br}$ and, from it by metathesis, $[\mathrm{NiIL^4}]\mathrm{I}$, $[\mathrm{Ni(NCS)_2L^4}]$, and $[\mathrm{NiBr(ClO_4)L^4}]$. The complexes fall into two groups.

The first group, containing $[\mathrm{Ni(NCS)_2L^4}]$ and $[\mathrm{NiBr(ClO_4)L^4}]$, we believe to contain six-co-ordinate nickel atoms. Thus the i.r. spectrum of the thiocyanate adduct is consistent with the presence of nitrogen-bonded NCS (broad bands at 2 060 and 472 $\mathrm{cm^{-1}}$) while the spectrum of the bromoperchlorate indicates the presence of unidentate perchlorate (doublet at 1 123 and 1 112, further bands at 1 050, 926, and another doublet at 625 and 618 cm^{-1}). The electronic spectra are recorded in Table 5.

TABLE 5

Ultraviolet–visible spectral data (250 to 2 000 nm) of $NiX_2{\cdot}L^4$ complexes measured by reflectance technique

Complex	Absorption bands/nm
$[NiBrL^4]Br$ [a]	1 198 ($^3E \leftarrow {}^3B_1$), 959 ($^1A_1 \leftarrow {}^3B_1$ weak band), 820 ($^3A_2$ or $^3B_2 \leftarrow {}^3B_1$), 574 ($^3E' \leftarrow {}^3B_1$); [b] $\mu_{eff.} = 2.75$ B.M.
$[NiIL^4]I$ [a]	1 300 ($^3E \leftarrow {}^3B_1$), 740 ($^3A_2$ or $^3B_2 \leftarrow {}^3B_1$), 574 ($^3E' \leftarrow {}^3B_1$); [b] $\mu_{eff.} = 2.72$ B.M.
$[NiBr(ClO_4)L^4]$ [c]	1 330, 959 [$^3T_{2g}(F) \leftarrow {}^3A_{2g}$], [d] 715 ($^1E_g \leftarrow {}^3A_{2g}$), 625, 574 (sh), 561 (sh) [$^3T_{1g}(F) \leftarrow {}^3A_{2g}$], [d] 388 [$^3T_{1g}(P) \leftarrow {}^3A_{2g}$]; [b] $\mu_{eff.} = 3.04$ B.M.; $Dq = 874$ cm^{-1}; $B = 1\ 103$ cm^{-1}
$[Ni(NCS)_2L^4]$ [c]	919, 830 [$^3T_{2g}(F) \leftarrow {}^3A_{2g}$], [d] 620 (sh) ($^1E_g \leftarrow {}^3A_{2g}$), 550 [$^3T_{1g}(F) \leftarrow {}^3A_{2g}$], 348 [$^3T_{1g}(P) \leftarrow {}^3A_{2g}$]; [b] $Dq = 1\ 146$ cm^{-1}; $B = 813$ cm^{-1}

[a] Assignments based upon high-spin square-pyramidal geometry. [b] Below this wavelength charge-transfer bands occur. [c] Assignments based upon an octahedral geometry. [d] Average of preceding wavelengths taken in calculation of *Dq* and *B*.

By use of the method of Lever,[18] values of *Dq* and *B* (Racah parameter) were calculated. The values obtained support the assignment of pseudo-octahedral geometry.

Considering the other two compounds, $[NiIL^4]I$ and $[NiBrL^4]Br$, we believe them to be five-co-ordinate pseudo-square-pyramidal in geometry. Attempts to assign the spectra to a six-co-ordinate system result in unrealistic values for *Dq* and *B*. The bromide $[NiBrL^4]Br$ has been previously assigned an octahedral geometry, on the evidence provided by its u.v.–visible spectrum.[11] However, the u.v.–visible spectrum we obtained differed from that previously reported. We did not observe the absorption reported at 943 nm, but instead two bands at 1 198 and 820 nm and a weak absorption at 959 nm.

The change in stereochemistry with anion for these nickel compounds is in agreement with the situation observed for the complexes based on $[NiL^3]^{2+}$.[17] One unusual result is the formation of a six-co-ordinate species involving the perchlorate anion in $[NiBr(ClO_4)L^4]$. However, molecular scale models of $[NiL^4]^{2+}$ indicate that there are two dissimilar ***trans*** sites for co-ordination of the anion and that it is, therefore, possible to co-ordinate the ClO_4^- ion.

We acknowledge the assistance of Mr. A. W. Johans with the *X*-ray crystallography and the S.R.C. for support (to K. M. R.).

[9/2010 *Received, 19th December,* 1979]

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