

In memory of S. M. Nelson

Studies involving Mixed Donor Macrocyclic Ligands. Comparative X-Ray Diffraction, Infrared, and Fast Atom Bombardment Mass Spectrometric Studies of the Nickel Thiocyanate Complexes of Three O₂N₃-Donor Macrocycles†

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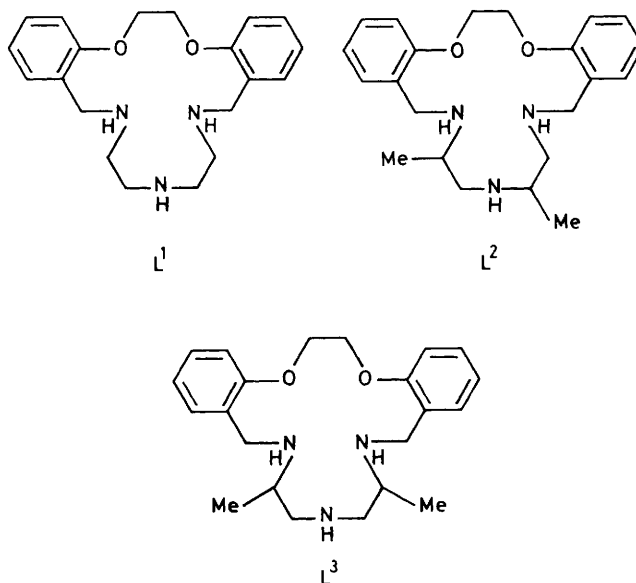
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Minor changes in the substitution pattern of the backbone of a 17-membered macrocyclic ring incorporating O₂N₃ donor atoms have been demonstrated to have a significant influence on the ligand co-ordination modes in the corresponding nickel thiocyanate complexes. Comparative i.r. and fast atom bombardment (f.a.b.) source mass spectrometry as well as X-ray diffraction studies (on three complexes) have been used to elucidate the nature of the species formed. A variety of structures occurs for these complexes: three of the complexes are monomeric and incorporate terminal isothiocyanato groups with the 1,4,7-triazaheptane macrocyclic fragment co-ordinating in either a facial or meridional manner. Two forms of the complex of the unsubstituted macrocycle were isolated. The more insoluble form is dimeric and incorporates unusual N-bridged isothiocyanato groups. The combination of i.r. and f.a.b. mass spectrometric studies has proven to be especially useful for structural elucidation in systems of the type investigated.

The heavy metal-ion chemistry of polydentate macrocyclic ligands containing both ether oxygen and amine donors has received considerable attention over recent years. For example, we have been especially concerned with the use of such macrocycles for metal-ion recognition studies.^{1,2} Nelson³ has also studied many examples of macrocyclic complexes from the above category as part of a wider investigation of the role of the metal ion in the template syntheses of such macrocyclic (Schiff base) systems.

The present paper describes the results of comparative X-ray diffraction, i.r., and fast atom bombardment (f.a.b.) mass spectrometric studies of the nickel thiocyanate complexes of the O₂N₃-donor macrocycles L¹—L³.

Other complexes of these ligands, including some nickel halide derivatives, have been the subject of earlier studies.^{2,4,5} An aim of this investigation was to study the effect of macrocycle substitution on the respective co-ordination geometries assumed by the complexes and to investigate the various thiocyanate bonding modes that may be present in the respective structures. Thus, in previous studies it has been demonstrated that minor variations in ligand substitution patterns may be reflected by major 'dislocations' in the co-ordination geometries adopted by the ligands. The study of such dislocations is of interest since, under favourable circumstances, they may be associated with unusual metal-ion discrimination behaviour.^{2,4,5}



Further, it was of interest to study the application of the f.a.b. technique to the study of co-ordination complexes of the present type. F.a.b. mass spectrometry is a technique of wide applicability for the study of fragile molecules as well as molecules of moderate to high molecular weight which are difficult to investigate by 'classical' mass spectrometric procedures.^{6,7} For example, the f.a.b. technique provides a means of ionizing otherwise non-volatile molecules (including

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salts). Although the study of inorganic systems has received less attention, f.a.b. investigations involving both organometallic and co-ordination compounds as well as large metal-containing polyoxoanions have been reported recently.^{7,8} It is clear that this technique shows considerable potential for the study of such systems.

Experimental

Preparation of NiL(NCS)₂·nH₂O [L = L¹—L³; n = 0, 0.5, or 1].—The macrocycle (1 mmol) in hot methanol was added to a stirred solution of nickel thiocyanate (1 mmol) in hot methanol. The respective products precipitated as the solution cooled; they were filtered off, washed sparingly with methanol,

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

Atom	x	y	z	Atom	x	y	z
<i>(a) [NiL¹(NCS)₂]₂·3MeOH</i>							
Ni ^a	8 283(12)	6 161(14)	-7 623(13)	C(10a)	-642(10)	-305(12)	-3 237(10)
N(1)	2 217(8)	518(10)	523(8)	C(1b)	4 318(11)	3 831(13)	-2 294(12)
C(1)	3 132(10)	643(11)	1 157(10)	O(1b)	3 599(6)	3 783(9)	-1 493(8)
S(1)	4 396(3)	811(4)	2 066(3)	C(2b)	3 414(10)	4 939(12)	-880(11)
N(2)	121(8)	1 323(9)	653(9)	C(3b)	3 869(11)	6 222(13)	-996(12)
C(2)	120(9)	2 298(13)	1 302(11)	C(4b)	3 593(11)	7 286(15)	-312(13)
S(2)	163(4)	3 714(4)	2 252(4)	C(5b)	2 985(11)	7 172(15)	451(13)
C(1a)	4 403(11)	2 490(13)	-2 821(12)	C(6b)	2 537(12)	5 919(13)	548(12)
O(1a)	3 309(6)	1 741(9)	-3 630(8)	C(7b)	2 768(10)	4 778(12)	-115(10)
C(2a)	3 214(10)	393(12)	-4 001(11)	C(8b)	2 351(10)	3 398(11)	79(10)
C(3a)	3 505(11)	-35(13)	-5 115(13)	N(1b)	1 432(6)	2 520(9)	-965(8)
C(4a)	3 323(11)	-1 397(13)	-5 558(13)	C(9b)	411(9)	3 090(11)	-1 316(10)
C(5a)	2 916(12)	-2 262(16)	-4 980(13)	C(10b)	-521(10)	2 036(11)	-2 340(10)
C(6a)	2 638(11)	-1 840(13)	-3 867(13)	N(1c)	-619(6)	687(8)	-2 126(6)
C(7a)	2 788(10)	-467(12)	-3 406(10)	C(1m)	1 222(11)	4 103(13)	5 822(12)
C(8a)	2 488(10)	29(12)	-2 225(11)	O(1m)	1 330(6)	2 823(9)	6 032(8)
N(1a)	1 294(6)	-360(8)	-2 292(6)	C(2m) ^b	4 513(27)	3 657(30)	3 809(27)
C(9a)	519(9)	-261(11)	-3 402(10)	O(2m) ^b	3 561(21)	3 831(23)	3 805(21)
<i>(b) [NiL²(NCS)₂(H₂O)]</i>							
Ni	971(2)	928(1)	1 484(1)	C(6a)	-6(12)	-1 610(11)	360(4)
S(1)	1 467(4)	3 752(3)	673(1)	C(7a)	-231(12)	-641(10)	508(4)
S(2)	2 040(4)	3 303(4)	2 336(1)	C(8a)	557(13)	-226(13)	796(4)
N(1)	1 000(11)	2 157(10)	1 146(3)	C(9a)	-473(12)	-857(11)	1 324(4)
N(2)	1 980(12)	1 733(11)	1 846(4)	C(10a)	417(13)	-1 275(11)	1 576(4)
O	2 657(9)	364(8)	1 275(3)	C(11a)	-75(13)	-2 204(12)	1 780(4)
N(1a)	-69(12)	61(8)	1 134(3)	C(1b)	-1 883(12)	2 607(11)	634(4)
N(1b)	-430(10)	1 407(8)	1 824(3)	C(2b)	-1 605(12)	3 203(10)	1 214(4)
N(1c)	954(11)	-433(8)	1 791(3)	C(3b)	-1 505(12)	4 216(11)	1 103(4)
C(1)	1 222(13)	2 818(12)	949(4)	C(4b)	-1 218(12)	4 993(12)	1 344(4)
C(2)	2 015(13)	2 381(12)	2 043(4)	C(5b)	-1 031(13)	4 759(13)	1 692(5)
O(1a)	-1 221(8)	909(6)	546(2)	C(6b)	-1 175(11)	3 730(10)	1 804(4)
O(1b)	-1 917(8)	2 409(6)	1 004(2)	C(7b)	-1 453(11)	2 946(10)	1 570(3)
C(1a)	-2 103(12)	1 593(12)	454(4)	C(8b)	-1 539(11)	1 818(9)	1 695(3)
C(2a)	-1 095(12)	-34(11)	379(4)	C(9b)	-650(12)	539(11)	2 084(4)
C(3a)	-1 780(13)	-360(12)	96(4)	C(10b)	392(11)	-154(11)	2 125(4)
C(4a)	-1 495(13)	-1 342(11)	-46(4)	C(11b)	-986(12)	982(11)	2 448(4)
C(5a)	-664(11)	-1 938(11)	65(4)				
<i>(c) [NiL³(NCS)₂]</i>							
Ni ^a	27 294(9)	18 922(7)	16 527(6)	C(6a)	2 060(9)	4 944(6)	2 429(6)
N(1)	1 084(6)	1 769(5)	906(4)	C(7a)	1 798(8)	4 111(6)	2 170(5)
C(1)	78(6)	1 758(5)	512(5)	C(8a)	1 932(9)	3 796(6)	1 355(6)
S(1)	-1 316(2)	1 752(2)	-48(1)	C(9a)	3 669(10)	3 177(6)	544(6)
N(2)	4 107(6)	2 041(4)	2 611(4)	C(10a)	4 614(9)	2 455(6)	582(6)
C(2)	5 106(8)	2 040(5)	2 986(5)	C(11a)	4 377(11)	4 016(8)	377(8)
S(2)	6 532(3)	2 056(2)	3 531(2)	C(1b)	391(9)	1 668(6)	3 420(6)
N(1a)	3 039(6)	3 194(4)	1 331(5)	C(2b)	1 358(8)	286(5)	3 317(5)
N(1b)	3 043(6)	533(4)	1 833(4)	C(3b)	1 202(8)	107(6)	4 137(5)
N(1c)	3 926(6)	1 676(5)	738(4)	C(4b)	1 566(9)	-728(6)	4 419(6)
O(1a)	1 137(6)	2 761(4)	2 542(4)	C(5b)	2 002(10)	-1 285(6)	3 921(6)
O(1b)	1 051(6)	1 063(4)	2 973(3)	C(6b)	2 144(9)	-1 088(6)	3 094(6)
C(1a)	18(9)	2 362(6)	2 831(5)	C(7b)	1 801(8)	-292(5)	2 790(5)
C(2a)	1 397(9)	3 583(6)	2 789(6)	C(8b)	1 925(8)	-58(5)	1 903(5)
C(3a)	1 286(9)	3 869(6)	3 592(6)	C(9b)	3 854(9)	229(6)	1 200(6)
C(4a)	1 548(10)	4 705(6)	3 780(6)	C(10b)	4 747(9)	937(6)	978(6)
C(5a)	1 915(9)	5 222(6)	3 195(6)	C(11b)	4 671(11)	-563(6)	1 487(8)

^a Fractional co-ordinates $\times 10^5$ for these nickel atoms. ^b Half occupancy.

and then dried over P_4O_{10} in vacuum before analysis; yields 40–60%.

The complex of L^1 , isolated and dried as just described, was obtained as its monohydrate (Found: C, 49.7; H, 5.5; N, 13.3. $C_{22}H_{29}N_5NiO_3S_2$ requires C, 49.5; H, 5.5; N, 13.1%). A second, less soluble, form of this complex also crystallized slowly (over 36 h) from the reaction filtrate as royal blue crystals; these crystals lost methanol of solvation on standing in air. The initial pale blue product (form 1) may be converted into this latter form (form 2) by slow recrystallization from methanol. Form 2 was used for the X-ray diffraction study without further drying. The crystalline product slowly crumbles in air with loss of methanol of solvation to yield a mid-blue powder. This mid-blue powder was further dried over P_4O_{10} in a vacuum. Dried in this manner, the product contained half a molecule of water for each monomeric unit present (the product is a dimer; see later) (Found: C, 50.1; H, 5.3; N, 12.9. $C_{44}H_{56}N_{10}Ni_2O_5S_4$ requires C, 50.3; H, 5.4; N, 13.3%).

The complexes of L^2 and L^3 yielded the following analytical data. Found for $NiL^2(NCS)_2 \cdot H_2O$: C, 51.1; H, 5.9; N, 12.2. $C_{24}H_{33}N_5NiO_3S_2$ requires C, 51.25; H, 5.90; N, 12.45%. Found for $NiL^3(NCS)_2$: C, 52.7; H, 5.8; N, 12.9. $C_{24}H_{31}N_5NiO_2S_2$ requires C, 52.95; H, 5.75; N, 12.8%. Crystals of these two complexes for the X-ray diffraction studies were obtained by recrystallization of the original products from methanol.

X-Ray Diffraction Studies.—X-Ray structures were obtained on crystals isolated as just described. The X-ray data were collected on a Philips PW1100 diffractometer using Mo- K_α radiation ($\lambda = 0.71069 \text{ \AA}$) as outlined previously.⁹ Major calculations were performed using SHELX 76.¹⁰

Crystal data for $[NiL^1(NCS)_2]_2 \cdot 3MeOH$. $C_{47}H_{66}N_{10}Ni_2O_7S_6$, $M = 1110.77$, triclinic, space group $P\bar{1}$, $a = 12.512(3)$, $b = 10.558(2)$, $c = 11.492(2) \text{ \AA}$, $\alpha = 100.87(2)$, $\beta = 104.39(2)$, $\gamma = 100.23(2)^\circ$, $U = 1403.4 \text{ \AA}^3$, $D_c = 1.31 \text{ g cm}^{-3}$, $Z = 1$, $F(000) = 594$, $R = 0.087$ for 2583 reflections [$I/\sigma(I) > 3.0$] (the methanol molecules are disordered).

Crystal data for $[NiL^2(NCS)_2(H_2O)]$. $C_{24}H_{33}N_5NiO_3S_2$, $M = 562.39$, orthorhombic, space group $Pbca$, $a = 11.686(3)$, $b = 12.796(3)$, $c = 38.196(6) \text{ \AA}$, $U = 5711.6 \text{ \AA}^3$, $Z = 8$, $D_c = 31 \text{ g cm}^{-3}$, $F(000) = 2368$, $R = 0.067$ for 1501 reflections [$I/\sigma(I) > 2.5$].

Crystal data for $[NiL^3(NCS)_2]$. $C_{24}H_{31}N_5NiO_2S_2$, $M = 544.38$, monoclinic, space group $P2_1/c$, $a = 10.333(3)$, $b = 15.811(4)$, $c = 16.238(4) \text{ \AA}$, $\beta = 96.61(2)$, $U = 2635.25 \text{ \AA}^3$, $D_c = 1.37 \text{ g cm}^{-3}$, $Z = 4$, $F(000) = 1144$, $R = 0.075$ for 2438 reflections [$I/\sigma(I) > 3.0$].

Weights were applied to individual data as $w = 1/[\sigma(F_o)]^2$. Table 1 lists non-hydrogen atom co-ordinates for the three structures; atom labelling follows that given in Figure 1. Selected bond distances and bond angles are given in Table 2.

Other Physical Measurements.—Positive-ion f.a.b. source mass spectra were determined using a JEOL JMS-DX300 spectrometer. Samples were milled with an ethanol-glycerol mixture or with 3-nitrobenzyl alcohol before insertion in the probe and fragmentation patterns were generally similar for each solvent system. An accumulation program was used to enhance resolution of the 'dimer' peak illustrated in Figure 2. Other physical measurements were performed as described previously.⁵

Results and Discussion

The interaction of macrocycles L^1 – L^3 with Ni^{II} thiocyanate in all cases yielded blue or green nickel complexes of stoichiometry $NiL(NCS)_2 \cdot nH_2O$ ($n = 0, 0.5$, or 1). All complexes are high-spin with 'normal' magnetic moments of 3.2–3.3 B.M. (Table 3). The respective molar conductances in

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

(a) $[NiL^1(NCS)_2]_2 \cdot 3MeOH$			
Ni–N(1)	2.014(9)	Ni–N(2)	2.177(11)
Ni–N(1a)	2.128(9)	Ni–N(1b)	2.095(10)
Ni–N(1c)	2.104(8)		
N(2)–Ni–N(1)	90.2(0.4)	N(1b)–Ni–N(1)	98.0(0.4)
N(1a)–Ni–N(1)	94.7(0.4)	N(1b)–Ni–N(2)	93.5(0.4)
N(1a)–Ni–N(2)	170.4(0.3)		
N(1b)–Ni–N(1a)	94.0(0.4)	N(1c)–Ni–N(2)	90.7(0.4)
N(1c)–Ni–N(1)	179.0(0.4)	N(1c)–Ni–N(1b)	82.5(0.3)
N(1c)–Ni–N(1a)	84.4(0.3)	C(2)–N(2)–Ni	140.8(1.0)
C(1)–N(1)–Ni	166.0(1.0)		
(b) $[NiL^2(NCS)_2(H_2O)]$			
Ni–N(1)	2.03(1)	Ni–N(2)	2.09(1)
Ni–O	2.246(9)	Ni–N(1c)	2.10(1)
Ni–N(1a)	2.12(1)	Ni–N(1b)	2.18(1)
N(2)–Ni–N(1)	91.8(0.5)	N(1b)–Ni–N(1a)	95.3(0.4)
N(1a)–Ni–N(1)	90.7(0.5)	N(1b)–Ni–N(1)	100.0(0.4)
N(1a)–Ni–N(2)	177.4(0.5)	N(1b)–Ni–N(2)	83.8(0.5)
N(1c)–Ni–N(1)	174.4(0.4)	N(1c)–Ni–N(2)	92.6(0.5)
N(1c)–Ni–N(1a)	84.9(0.4)	N(1c)–Ni–N(1b)	83.9(0.4)
O–Ni–N(1)	90.4(0.4)	O–Ni–N(2)	84.2(0.4)
N(1a)–Ni–O	96.2(0.4)	N(1b)–Ni–O	164.3(0.4)
N(1c)–Ni–O	86.5(0.4)		
C(1)–N(1)–Ni	167.8(1.4)	C(2)–N(2)–Ni	146.1(1.5)
(c) $[NiL^3(NCS)_2]$			
Ni–N(1)	1.981(6)	Ni–N(2)	1.998(6)
Ni–N(1a)	2.156(7)	Ni–N(1b)	2.188(6)
Ni–N(1c)	2.067(7)		
N(2)–Ni–N(1)	166.5(0.3)	N(1b)–Ni–N(1a)	161.1(0.3)
N(1a)–Ni–N(1)	94.9(0.3)	N(1b)–Ni–N(1)	95.1(0.3)
N(1a)–Ni–N(2)	87.9(0.3)	N(1b)–Ni–N(2)	86.0(0.3)
N(1c)–Ni–N(1)	95.0(0.3)	N(1c)–Ni–N(2)	98.5(0.3)
N(1c)–Ni–N(1a)	82.3(0.3)	N(1c)–Ni–N(1b)	80.9(0.3)
C(1)–N(1)–Ni	173.7(0.7)	C(2)–N(2)–Ni	159.8(0.7)

Table 3. Magnetic, i.r., and f.a.b. mass spectral data for the complexes

Complex	$\mu_{\text{eff.}}^a / \text{B.M.}$	$\nu_{\text{NC}}^b / \text{cm}^{-1}$	m/z		
			$[NiL]^+$	$[Ni(NCS)]^+$	$[Ni_2L_2(NCS)_3]^+$
$[NiL^1(NCS)_2] \cdot H_2O$	3.24	2100 (br)	399	457	
$[NiL^1(NCS)_2]_2 \cdot H_2O$	3.17	2088, 2015	399	457	972
$[NiL^2(NCS)_2(H_2O)]$	3.28	2089, 2061	427	485	
$[NiL^3(NCS)_2]$	3.22	2093, 2074	427	485	

^a At 295 K; B.M. = $0.927 \times 10^{-23} \text{ A m}^{-2}$. ^b Nujol mull.

methanol (complex concentration $\sim 10^{-3} \text{ mol dm}^{-3}$) were in each case less than the value expected for a 1:1 electrolyte in this solvent; thus the tendency for the (co-ordinated) thiocyanates to dissociate in solution is small. Solid-state (Nujol mull) spectra in the visible-near-i.r. region tended to be not well resolved but were consistent with all complexes being high-spin and containing distorted five- or six-co-ordinate geometries.

F.A.B. Source Mass Spectrometry.—Positive-ion f.a.b. mass spectrometry gave similar fragmentation patterns for the two

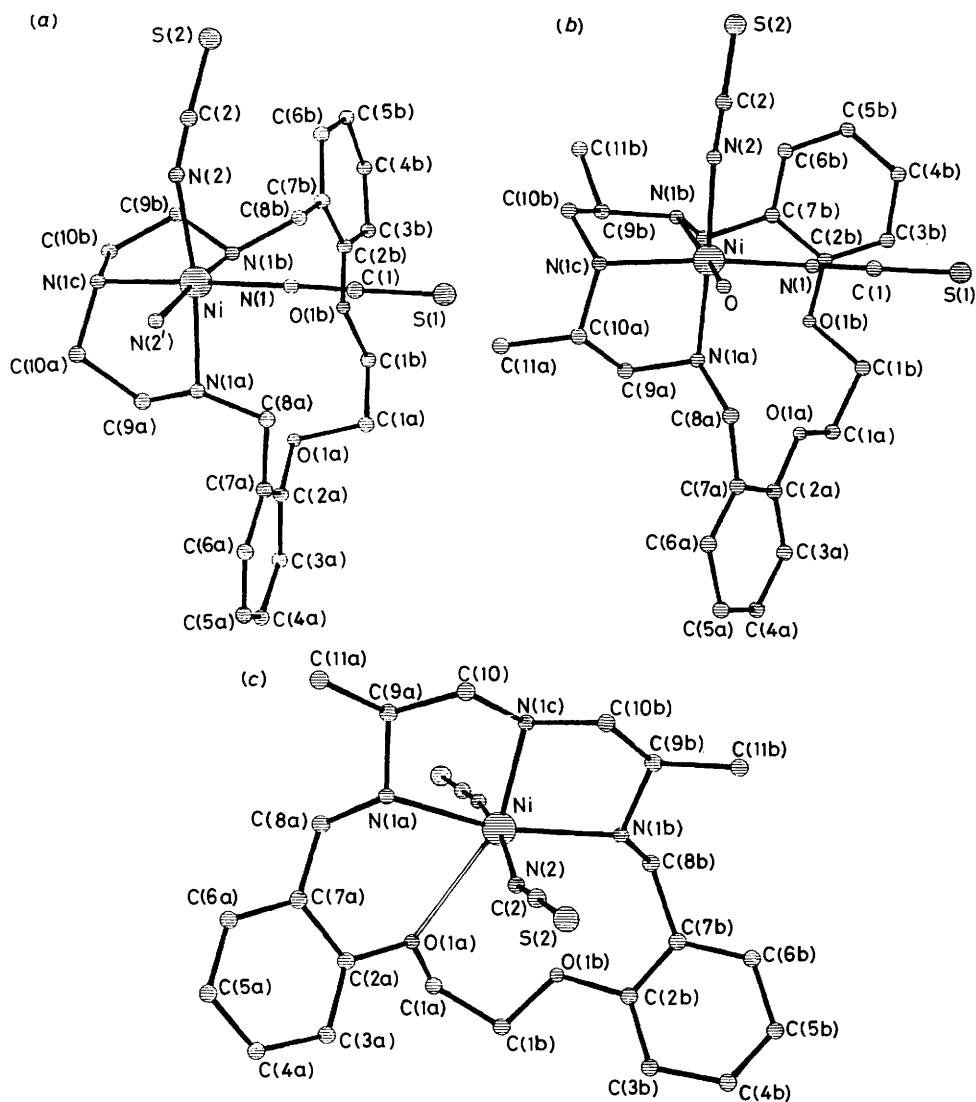


Figure 1. The structures of the nickel(II) complexes (a) $[\{\text{NiL}^1(\text{NCS})_2\}_2] \cdot 3\text{MeOH}$ (monomeric unit), (b) $[\text{NiL}^2(\text{NCS})_2(\text{H}_2\text{O})]$, and (c) $[\text{NiL}^3(\text{NCS})_2]$

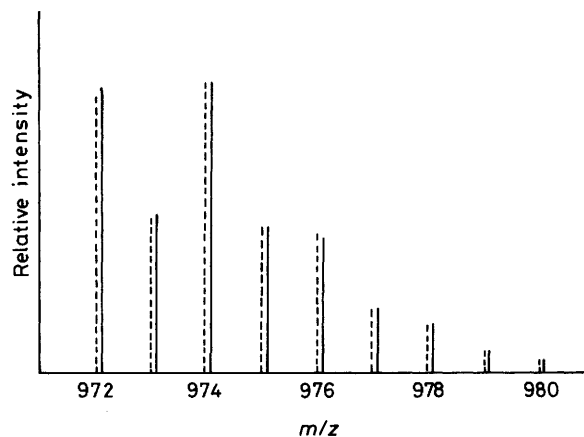


Figure 2. The calculated *versus* the observed mass spectral isotopic distribution pattern for the $[\text{Ni}_2(\text{L}^1)_2(\text{NCS})_3]^+$ ion

(dimethyl-substituted) complexes derived from L^2 and L^3 . Although no molecular ion was observed for these species under the conditions employed, prominent peaks corresponding to

$[\text{NiL}(\text{NCS})]^+$ and $[\text{NiL}]^+$ were evident in each spectrum (Table 3). Corresponding peaks to these also occurred for both forms of the complex of L^1 ; however, the spectrum of the more insoluble isomer (form 2) contains a further peak at m/z 972 corresponding to the $[\text{Ni}_2(\text{L}^1)_2(\text{NCS})_3]^+$ ion. The calculated *versus* the observed isotopic distribution patterns for this ion are illustrated in Figure 2. Thus the f.a.b. data are consistent with form 2 of the complex of L^1 having a dimeric structure whereas each of the other complexes are suggested to be monomeric.

I.r. Spectrophotometric Studies.—I.r. spectral data using Nujol mulls were obtained for all complexes. The spectra confirmed the presence of water when it was suggested to be present by the analytical data. The spectrophotometric data for the ν_{NC} region (Table 3) are consistent with the presence of terminal (N-bonded) thiocyanate groups in all complexes:¹¹ each species exhibited either one or two bands in the region 2 100–2 060 cm^{-1} . Although the C–S stretching frequency (in the region 860–690 cm^{-1}) is usually more useful for differentiating S-bonded from N-bonded thiocyanates,^{11,12} for the present complexes the presence of ligand bands in this region made assignment of the respective C–S stretches difficult. The spectrum of form 2 of the complex of L^1 is of special interest

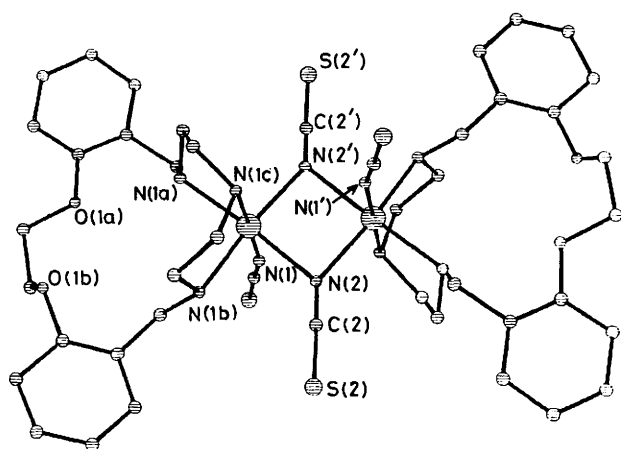
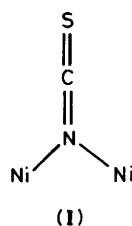


Figure 3. The dimeric structure of $[\{\text{NiL}^1(\text{NCS})_2\}_2]$



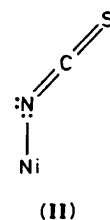
(I)

since it also contains a 'low' ν_{NC} stretching resonance at 2015 cm^{-1} . Such a value for this stretch is unusual although similar values have been documented for a very limited number of heavy-metal complexes.^{13,14} The position of this peak strongly indicates the presence of one or more N-bridging thiocyanates spanning nickel centres [see (I)]. The thiocyanato nitrogen atom may be considered to be effectively sp^2 hybridized in such an arrangement. The f.a.b. spectral data taken together with the i.r. data thus strongly suggest that form 2 of the complex of L^1 is a N-bridged thiocyanato dimer (which also contains N-terminal thiocyanato functions). In order to investigate further the structure of this complex, as well as of the complexes of L^2 and L^3 , X-ray diffraction studies were carried out on each of these compounds.

Molecular Structure of $[\{\text{NiL}^1(\text{NCS})_2\}_2]$ (Form 2).—Form 2 of the complex of L^1 does exhibit a N-bridged thiocyanato (dimeric) structure (Figure 3) with the Ni–Ni distance being 3.03 \AA ; Figure 1(a) illustrates one half of the centrosymmetric dimeric unit. In this complex each Ni^{II} achieves a pseudo-octahedral geometry with the oxygen atoms of L^1 not co-ordinating. Each Ni^{II} co-ordination shell contains the three nitrogens of L^1 (in a facial arrangement) together with one nitrogen from a terminal isothiocyanato group and two N-bridging isothiocyanato groups. Thus, each nickel atom achieves its normal co-ordination number of six by using only nitrogen donors; the non-co-ordination of the ether oxygens is not unexpected since the affinity of such donors for Ni^{II} is not high and, in another Ni^{II} compound, non-co-ordination of such groups has been confirmed by X-ray diffraction.¹⁵

The macrocyclic Ni–N bond lengths (Table 2) are unexceptional and fall close to the mean length of 2.11 \AA found for 89 secondary amine to high-spin Ni^{II} bonds reported in the literature.^{1,16}

Although bridging thiocyanato ligands are relatively common, usually the bridging mode involves both nitrogen and sulphur such that a M–NCS–M linkage occurs.¹⁷ Bridging via



(II)

sulphur has also been observed,¹⁸ although this, like bridging solely through nitrogen, is quite rare. However, of significance to the present structure is the recently reported trinuclear Ni^{II} complex which incorporates both N-bridging thiocyanato ligands as well as bridging thiazole ligands.¹⁴ This compound was the first reported Ni^{II} complex to contain thiocyanate bridged in this manner and exhibits Ni–Ni distances of 3.39 \AA .

Molecular Structure of $[\text{NiL}^2(\text{NCS})_2(\text{H}_2\text{O})]$.—The unsymmetrical dimethyl derivative L^2 also yields a complex in which the ether oxygen donors are not co-ordinated [Figure 1(b)]. However, in this case the compound is monomeric; the pseudo-octahedral geometry is achieved by co-ordination of the three nitrogens of L^2 , two *cis* (terminal) N-bonded isothiocyanato ligands, and a water molecule. Once again, the 1,4,7-triazaheptane unit of the macrocycle co-ordinates in a facial manner. As in the previous structure, the Ni–N distances in the present case fall within the range for such bonds in octahedral complexes^{1,16} even though the Ni–N(1b) distance, at $2.18(1) \text{ \AA}$, is near the top end of the range.

Molecular Structure of $[\text{NiL}^3(\text{NCS})_2]$.—The symmetrically substituted *meso* macrocycle L^3 gives a complex in which the co-ordination geometry is very irregular [Figure 1(c)]. In this structure the three nitrogens of L^3 co-ordinate to Ni^{II} in a *mer* configuration with the ether oxygens also lying approximately in this co-ordination plane. However, the latter donors [O(1a) and O(1b)] are 2.67 and 3.19 \AA respectively from Ni^{II} . Both these lengths are longer than usually observed for high-spin Ni^{II} to ether bonds; more commonly, such bonds fall in the range 2.0 – 2.3 \AA .¹⁶ The closer of the above oxygens may be considered to have a weak interaction with the metal. Once again, the structure provides clear evidence for the low affinity of ether donors for high-spin Ni^{II} mentioned previously.

As before, the macrocyclic Ni–N bonds (Table 2) fall in the range expected for secondary amine to high-spin Ni^{II} in other systems. A molecular model of this complex suggests that the co-ordination stereochemistry adopted may, in part, be a reflection of the positions of methyl substitution on the N_3 -backbone; steric clashes involving these groups appear to inhibit facial co-ordination in this case.

It is interesting that the terminal M–NCS linkages in this complex, as indeed also occurs in the two complexes just discussed, are in each case bent (Table 2) with M–N–C angles in the range 141 – 174° . In other systems it has been established that this linkage may be either linear or angular (with examples of M–N–C angles falling even lower than 141° having been documented).^{19,20} Although non-linearity of this type may be induced by steric effects,²¹ it also commonly appears to reflect electron density localization on the donor nitrogen such that a canonical form of type (II) contributes to the structure adopted.^{19,22}

Concluding Remarks.—The X-ray studies of all three complexes are in complete accord with the inferences drawn from the i.r. and f.a.b. studies and hence confirm the usefulness of the latter for investigations of the present type. The studies also illustrate how apparently minor changes in macrocyclic

ligand structure may influence alternative modes of ligand coordination. As mentioned already, similar induced structural changes have been used to control metal-ion recognition behaviour within other series of macrocyclic-ligand systems.

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