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Interaction of Cobalt(II), Nickel(II), and Copper(II) with a New Macrocyclic Ligand Incorporating O₄N₄ Heteroatoms. Synthetic, Solution, and X-ray Diffraction Studies

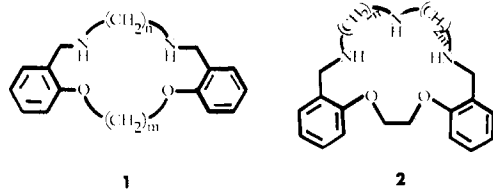
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The interaction of cobalt(II), nickel(II), and copper(II) with a new 28-membered O₄N₄ macrocycle (L) has been investigated, and 1:1 complexes with each of these metal ions have been isolated. From physical measurements, the cobalt(II) and nickel(II) complexes have been assigned octahedral or pseudooctahedral geometries. Potentiometric studies on these complexes in 95% methanol ($I = 0.1$, (CH₃)₄NCl) indicate log K values for the equilibrium $M^{2+} + L \rightleftharpoons ML^{2+}$ of 10.13 ± 0.10 for cobalt and 12.6 ± 0.09 for nickel. These values are higher than those obtained for the corresponding complexes of related 17- and 18-membered O₂N₃-donor macrocycles. The trends in the respective log K values indicate coordination of all four nitrogens of the 28-membered macrocycle to the above metal ions. An X-ray diffraction study of NiL(NCS)₂ (dimethylformamide) has been undertaken. The nickel ion has a N₆-coordination sphere with the four nitrogens of the macrocycle and the two thiocyanate nitrogens coordinating in a pseudooctahedral arrangement. The two thiocyanate ligands occupy cis positions: space group $Pbcn$, $a = 20.268$ (3) Å, $b = 12.236$ (2) Å, $c = 17.443$ (3) Å, $R = 0.053$ for 1827 four-circle diffractometer data with $I > 3\sigma(I)$. The other noncrystallographic studies for this complex are thus consistent with the X-ray structure.

Introduction

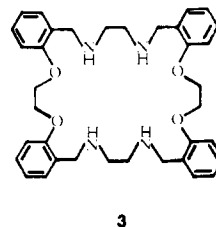
In contrast to the metal ion chemistry of macrocyclic ligands incorporating all ether-oxygen or all nitrogen donor atoms, the chemistry of mixed oxygen-nitrogen donor macrocycles has received less attention.² As part of a program involving the study of such macrocycles as potential metal-ion selective reagents, synthetic, structural, kinetic, and thermodynamic aspects of the interaction of macrocycles of types 1 and 2 with



cobalt(II), nickel(II), and copper(II) have been investigated.³⁻¹⁰

A potentially useful macrocyclic ring-size effect was observed on interaction of nickel with the macrocycles of type 1,⁶ along this series of 14- to 17-membered macrocycles, a peak in the thermodynamic stabilities occurred at the 16-membered ring complex. With cobalt(II) or copper(II), no clearly defined ring-size discrimination effects were observed and this difference has been rationalized in terms of the proposed structures of these complexes.^{7,8}

As an extension of these previous studies, we now discuss the results of an investigation involving the interaction of the larger-ring macrocycle 3 (incorporating eight potential donor atoms) with cobalt(II), nickel(II), and copper(II).



- (1) (a) James Cook University. (b) ETH, Zurich. (c) Polytechnic of North London.
- (2) Izatt, R. M.; Christensen, J. J., Eds. "Synthetic Multidentate Macrocyclic Compounds"; Academic Press: New York, 1978. Lindoy, L. F. *Chem. Soc. Rev.* **1975**, *4*, 421.
- (3) Armstrong, L. G.; Grimsley, P. G.; Lindoy, L. F.; Lip, H. C.; Norris, V. A.; Smith, R. J. *Inorg. Chem.* **1978**, *17*, 2350.
- (4) Ekstrom, A.; Lindoy, L. F.; Lip, H. C.; Smith, R. J.; Goodwin, H. J.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1027.
- (5) Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *Inorg. Chem.* **1980**, *19*, 724.
- (6) Anderegg, G.; Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 2670. Adam, K. R.; Lindoy, L. F.; Smith, R. J.; Anderegg, G.; Henrick, K.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Chem. Commun.* **1979**, 812.
- (7) Adam, K. R.; Anderegg, G.; Lindoy, L. F.; Lip, H. C.; McPartlin, M.; Rea, J. H.; Smith, R. J.; Tasker, P. A. *Inorg. Chem.* **1980**, *19*, 2956.
- (8) Lindoy, L. F.; Lip, H. C.; Rea, J. H.; Smith, R. J.; Henrick, K.; McPartlin, M.; Tasker, P. A. *Inorg. Chem.* **1980**, *19*, 3360.
- (9) Adam, K. R.; Lindoy, L. F.; Lip, H. C.; Rea, J. H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1980**, 74. Adam, K. R.; Lindoy, L. F.; Lip, H. C.; Smith, R. J.; unpublished work.
- (10) This "dimeric" product was originally erroneously assumed to have a "monomeric" structure of type 1 ($m = n = 2$)—see: Grimsley, P. G.; Lindoy, L. F.; Lip, H. C.; Smith, R. J.; Baker, J. T. *Aust. J. Chem.* **1977**, *30*, 2095. However, the monomeric form can be isolated from the filtrate as its dihydrochloride and purified as described in the above reference; alternatively, the material remaining in the filtrate can be complexed to nickel chloride, the resulting complex recrystallized from methanol, and pure monomer obtained by addition of excess EDTA to an aqueous solution at pH 10 of the recrystallized complex. The free macrocycle which separates can be extracted into chloroform and isolated as its dihydrochloride on passing dry HCl through the chloroform extract.

Experimental Section

Synthesis and Characterization of the Complexes. Conductance measurements were determined with the use of a Philips conductivity bridge type PR 9500. All measurements were recorded at 25 °C on solutions of approximately 10^{-3} M. Infrared spectra were recorded with the use of Nujol mulls with a Perkin-Elmer 197 spectrophotometer. All spectra were calibrated with a polystyrene standard. Solution spectra (in dimethyl sulfoxide) were obtained with the use of a Beckman ACTA-IV spectrophotometer. Solid-state spectra were determined on the above spectrophotometer using mulls of the compound spread on filter paper. Magnetic moments were determined with the use of a Faraday balance calibrated against Hg[Co(NCS)₄]. ¹H NMR spectra were determined with a Jeol JHN-NM-100 spectrometer, and ¹³C spectra were obtained on a Jeol JNM FX-60Q spectrometer. The mass spectra were obtained with a Jeol JMS-D100 spectrometer and a Kratos MSS0 (field-desorption) spectrometer. We thank Dr. A. Dell of the Department of Biochemistry, Imperial College, London, for determining the field-desorption spectrum. Microanalyses for C, H, and N were determined by Mr. J. Kent, Department of Chemistry, University of Queensland. Metal analyses were determined using a Varian-AA6 atomic absorption spectrophotometer. All compounds gave satisfactory analytical data and these are listed in supplementary Table SI.

Spectrophotometric titrations were performed by direct incremental addition of known weights of the ligand to the spectrophotometric cell containing the respective metal perchlorates in dimethyl sulfoxide.

In the case of cobalt(II), all additions were carried out in a nitrogen atmosphere to inhibit formation of the corresponding cobalt(III) species.

3,4,9,10,17,18,23,24-Tetrabenzo-1,12,15,26-tetraaza-5,8,19,22-tetraoxacyclooctacosane (3). To a stirred, warm solution of 1,4-bis(2-formylphenyl)-1,4-dioxabutane³ (2.7 g, 0.01 mol) in dry methanol (200 mL) was slowly added ethane-1,2-diamine (0.60 g, 0.01 mol) in dry methanol (50 mL). After addition of borax (0.5 g), sodium borohydride (1.0 g) was slowly added. The solution was concentrated to 100 mL and allowed to cool, whereupon the product separated as a white solid.¹⁰ It was filtered off and twice recrystallized from ethyl acetate and then washed with ether: yield 30%; mp (uncor) 168 °C; mass spectral parent ion *m/e* 596 (a field-desorption mass spectrum confirmed the absence of any of the corresponding "monomeric" macrocycle with a *m/e* of 298 as no peak corresponding to this ratio was present); ¹H NMR (CDCl₃, referenced from tetramethylsilane) δ 1.97 (s, NH), 2.65 (s, NCH₂), 3.74 (s, aromatic CH₂), 4.31 (s, OCH₂), 6.80–7.30 (m, aromatic), ¹³C{H} NMR (dimethyl-*d*₆ sulfoxide, referenced from tetramethylsilane) δ 47.47 (NCH₂), 48.35 (aromatic CH₂), 66.43 (OCH₂), 111.37, 120.11, 127.34, 128.61, 128.92, 155.87 (C₆H₄). Anal. Calcd for C₃₆H₄₄N₄O₄: C, 72.5; H, 7.4; N, 9.4. Found: C, 72.3; H, 7.5; N, 9.2.

Preparation of the Complexes. Ligand **3** (1 mmol) in hot methanol or butanol was added slowly to a hot stirred solution of the required metal salt (1 mmol) in methanol or butanol. The solution was allowed to cool, and the product which formed was filtered off, washed with methanol, and dried over P₂O₅ in vacuo.

log *K* Determinations. The apparatus and conditions (95% methanol; *I* = 0.1, (CH₃)₄NCl) for determination of the stability constants were identical with those used previously for analogous studies involving complexes of ligands of type **1** and **2**.⁶ The apparatus was calibrated daily to yield *E*₀ and p*K*_w values for the system by titration of a solution containing HCl (4.00 × 10⁻³ M) and recrystallized tetramethylammonium chloride (0.1 M; Fluka, puriss) in 95% methanol with standardized tetramethylammonium hydroxide (0.1 M) in 95% methanol. All determinations were carried out at 25.0 ± 0.05 °C.

log *K* values for the complexes were obtained by titration of a solution containing macrocycle (~10⁻³ M) and metal ion ((0.5–2.8 × 10⁻³ M) in calibration solution with tetramethylammonium hydroxide (0.1 M). The protonation constants for **3** were determined by a similar procedure using only a solution of the macrocycle. All values are the mean from three to six separate determinations. Titration steps of between 0.02 and 0.2 mL were chosen such that the millivolt changes between successive points did not exceed 10 mV. log *K* values were calculated with use of the program "KONST",¹¹ and a range of data were also processed with use of the program "MINIQUAD".¹² Both programs yielded values which were identical within experimental error.

X-ray Structure Determination. Light blue-purple prisms of [NiL(NCS)₂]₂·DMF were obtained by slow evaporation of a solution of [NiLCl₂] in CH₃OH/DMF to which had been added a slight excess of NH₄NCS in H₂O. Crystal data: C₄₁H₅₁N₇NiO₅S₂, mol wt 844.75, orthorhombic, space group *Pbcn*, *a* = 20.268 (3) Å, *b* = 12.236 (2) Å, *c* = 17.443 (3) Å, ¹³*U* = 4325.8 Å³, *T* = 22 °C, *Z* = 4, *d*(calcd) = 1.298 g cm⁻³, μ(Mo Kα) = 5.46 cm⁻¹.

Data were collected on a crystal of dimensions ca. 0.32 × 0.30 × 0.26 mm with use of a Philips PW1100 four-circle diffractometer and graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). A θ–2θ scan mode was used, and reflections with 3 < θ < 25° in one octant were examined. The method of data collection and calculation of reflection intensities was similar to that described previously.^{7,8} *I* and σ(*I*) were corrected for Lorentz and polarization factors and semiempirical absorption corrections based on a pseudoellipsoid model¹⁴ were made. A total of 429 azimuthal scan data from eight independent reflections were used, and relative transmission factors ranged from 1.0 to 0.817 for the full data set. Reflections for which *I* < 3σ(*I*) were rejected, and equivalent reflections were averaged to give 1827 unique data.

Structure Solution and Refinement. The structure was solved by multiresolution Σ₂ sign expansion for terms with *E* > 1.4. The Ni atom on the twofold axis and the NCS group were located from the *E* map with the highest combined figure of merit. The remaining nonhydrogen atoms were located from a subsequent difference synthesis. Two atoms of the DMF molecule, N(1s) and O(1s), lie on a crystallographic twofold axis; therefore, the other solvent atoms were treated as disordered and assigned site occupancy factors of 0.5. The *R* factor after four cycles of refinement with isotropic thermal parameters for the nonhydrogen atoms was 0.12. The thermal parameters for the atoms C(1a) and C(1b) were large; a difference Fourier map calculated without these atoms revealed a somewhat extended region of electron density for each atom. Although this is consistent with some conformational disorder of the ethane bridge -C(1a)–C(1b)-, it was not possible to resolve the maxima of electron density into separate components. A difference Fourier map calculated at this stage showed maxima corresponding to reasonable positions for all hydrogen atoms except those attached to atoms C(1a) and C(1b) and those of the DMF molecule. In the final stages of refinement, the secondary amine hydrogen atoms were refined isotropically, and the remaining hydrogen atoms (excluding those of the solvent molecule) were included in calculated positions, "riding" on the carbon atoms to which they are bonded at a fixed distance of 0.95 Å. A common isotropic thermal parameter was assigned to the phenylene hydrogen atoms and another to the methylene hydrogen atoms. These two parameters were included as free variables, giving values of 0.094 and 0.084 Å², respectively, after six cycles of refinement in which all nonhydrogen atoms were assigned anisotropic thermal parameters. This resulted in *R* = 0.0534, *R*_w = 0.0552 [*R*_w = Σw^{1/2}||*F*_o| - ||*F*_c||/Σw^{1/2}||*F*_o||], where *w* was the weight assigned to each reflection as *w* = 1/σ²(*F*_o). The final difference Fourier map showed diffuse regions of electron density with intensities <0.45 e Å⁻³ in the region of the disordered DMF molecule, the C(1a) and C(1b) atoms (see above), and the Ni atom.

Major computations were performed with the SHELX program.¹⁵ The neutral-atom scattering factors used¹⁶ were corrected for both the real and imaginary anomalous scattering contributions.¹⁷ Atomic positional and thermal parameters are given in Table I.

Results and Discussion

Synthesis and Characterization of the Complexes. The 28-membered macrocycle **3** is formed as a crystalline solid during the synthesis of the corresponding monomeric (14-membered) macrocycle (**1**, *n* = 2, *m* = 2).^{18,19} Reaction of **3** with the appropriate metal salt in methanol or butanol leads to isolation of a range of complexes of type [M(ligand)₂]_n·*n*H₂O (where M = Co, Ni, or Cu; X = Cl, Br, NCS, or ClO₄; *n* = 0, 1/2, or 1). The complexes are characterized by low solubility in most organic solvents. Physical data for the complexes are summarized in Table II. The magnetic moments of all complexes fall in the ranges expected for the corresponding high-spin cases. The infrared spectra of all complexes show (secondary) amine stretching modes in the region 3370–3260 cm⁻¹ and also confirmed the presence of water where it was suggested to be present from the analytical data. The complexes with perchlorate anions each showed a split perchlorate stretching absorption at ~1100 cm⁻¹. This splitting could reflect different perchlorate environments in these complexes arising from crystal packing or hydrogen-bonding effects, or it may indicate a lowering of the symmetry of the perchlorate group because of coordination to the metal

(11) Anderegg, G. *Helv. Chim. Acta* **1961**, *44*, 1673.
 (12) Gans, P.; Sabatini, A.; Vacca, A. *Inorg. Chim. Acta* **1976**, *18*, 237.
 (13) Unit cell parameters were obtained from a least-squares fit of the setting angles of 25 reflections with 2θ values of ca. 20°.
 (14) Sheldrick, G. M. EMPABS program, University Chemical Laboratory, Cambridge CB2 1EW, U.K., 1976.

(15) Sheldrick, G. M. SHELX-76 program system, University Chemical Laboratory, Cambridge, CB2 1EW, U.K., 1976.
 (16) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 390.
 (17) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
 (18) An analogous 28-membered N₄-donor macrocycle has also been synthesized with use of a similar (nontemplate) procedure: Owston, P. G.; Peters, R.; Tasker, P. A., unpublished work.
 (19) Examples of related "double" ring Schiff base macrocycles produced by template synthesis using ions such as Ag(I) or Pb(II) have also been reported recently: Drew, M. G. B.; Rodgers, A.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1978**, 415. Drew, M. G. B.; McFall, S. G.; Nelson, S. M. *J. Chem. Res., Synop.* **1979**, 16.

Table I. Refined Atomic Positional and Thermal Parameters for $[\text{NiL}(\text{NCS})_2] \cdot \text{DMF}$

atom	x^a	y	z	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0	4899 (1)	2500	285 (6)	343 (7)	384 (5)	0	-10 (7)	0
N	244 (3)	3758 (5)	3319 (4)	48 (4)	43 (4)	48 (4)	-2 (3)	-7 (4)	9 (3)
C	569 (4)	3261 (7)	3720 (4)	34 (5)	73 (6)	41 (5)	-2 (4)	13 (4)	6 (4)
S	1052 (1)	2549 (3)	4277 (2)	74 (2)	177 (2)	74 (2)	62 (2)	2 (2)	47 (2)
C(1a)	2677 (6)	5964 (11)	2756 (11)	80 (9)	166 (12)	382 (33)	6 (9)	-34 (15)	-180 (18)
O(1a)	2340 (3)	5037 (6)	2656 (4)	50 (4)	86 (5)	129 (6)	3 (4)	-20 (4)	-41 (5)
C(2a)	2514 (5)	4456 (8)	2017 (6)	46 (5)	59 (6)	92 (7)	11 (5)	3 (6)	-1 (6)
C(3a)	3160 (5)	4409 (8)	1714 (7)	40 (6)	81 (7)	132 (10)	-4 (5)	4 (6)	12 (7)
C(4a)	3274 (6)	3756 (10)	1108 (7)	64 (8)	129 (11)	95 (9)	40 (8)	31 (7)	36 (8)
C(5a)	2794 (6)	3176 (11)	773 (6)	83 (8)	139 (12)	73 (7)	58 (8)	18 (7)	16 (7)
C(6a)	2160 (5)	3261 (9)	1050 (5)	56 (7)	116 (9)	77 (7)	33 (6)	14 (5)	-3 (6)
C(7a)	2008 (4)	3893 (7)	1682 (5)	48 (5)	56 (5)	55 (5)	10 (4)	5 (4)	5 (4)
C(8a)	1317 (4)	3889 (6)	2012 (5)	38 (5)	44 (5)	69 (6)	7 (4)	9 (4)	-5 (4)
N(1a)	990 (3)	4951 (5)	2076 (3)	29 (3)	41 (4)	48 (3)	-1 (4)	-1 (3)	-2 (4)
H(N1a) ^c	1188 (36)	5413 (55)	2349 (43)	$U_{\text{iso}} = 50 (26) \text{ \AA}^2$					
C(9a)	950 (4)	5511 (7)	1326 (5)	46 (5)	72 (6)	66 (6)	7 (5)	11 (4)	16 (5)
C(9b)	531 (4)	6488 (7)	1398 (5)	56 (6)	79 (7)	74 (7)	-1 (5)	10 (5)	33 (5)
N(1b)	-141 (3)	6179 (6)	1666 (4)	36 (5)	47 (4)	56 (4)	1 (4)	-4 (4)	0 (3)
H(N1b) ^c	-300 (38)	6676 (55)	1884 (41)	$U_{\text{iso}} = 49 (27) \text{ \AA}^2$					
C(8b)	-627 (3)	6003 (6)	1032 (4)	41 (5)	62 (5)	39 (4)	9 (4)	-8 (4)	-7 (4)
C(7b)	-927 (4)	7076 (7)	768 (4)	41 (5)	64 (5)	46 (5)	8 (4)	-5 (4)	5 (4)
C(6b)	-662 (5)	7678 (8)	174 (5)	78 (7)	100 (8)	59 (6)	18 (6)	11 (5)	20 (5)
C(5b)	-946 (6)	8672 (9)	-37 (6)	123 (10)	114 (10)	109 (9)	27 (8)	27 (9)	82 (8)
C(4b)	-1501 (6)	9059 (9)	319 (7)	130 (11)	106 (9)	122 (10)	57 (9)	33 (9)	72 (8)
C(3b)	-1771 (5)	8464 (8)	901 (6)	89 (9)	94 (8)	93 (8)	50 (7)	15 (7)	29 (7)
C(2b)	-1484 (4)	7482 (7)	1121 (5)	54 (6)	68 (6)	61 (5)	14 (5)	3 (4)	20 (5)
O(1b)	-1741 (3)	6884 (5)	1728 (3)	56 (4)	82 (4)	97 (4)	19 (3)	23 (4)	34 (3)
C(1b)	-2390 (5)	6691 (10)	1650 (8)	41 (8)	167 (10)	352 (20)	33 (7)	44 (10)	136 (11)
C(1s) ^d	156 (18)	1186 (14)	2383 (37)	75 (32)	.52 (11)	295 (52)	3 (12)	53 (24)	22 (21)
C(2s) ^d	305 (12)	-123 (21)	3404 (13)	110 (18)	108 (18)	102 (16)	-15 (16)	-11 (14)	-32 (16)
N(1s)	0	75 (10)	2500	88 (9)	44 (7)	182 (14)	0	-28 (12)	0
C(3s) ^d	-116 (13)	-746 (16)	2169 (15)	73 (20)	63 (13)	151 (27)	7 (13)	10 (18)	-20 (14)
O(1s)	0	-1697 (8)	2500	152 (12)	56 (7)	179 (12)	0	29 (10)	0

^a Fractional coordinates $\times 10^4$. The standard deviation of the least significant digit is included in parentheses in this and subsequent tables. ^b Values $\text{\AA} \times 10^3$ (except for Ni; $\text{\AA} \times 10^4$) expressed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. ^c These atoms were refined isotropically. ^d Site occupation factors for these atoms is 0.5.

Table II. Physical Data for the Complexes of 3

compound	color	Λ^a/S $\text{cm}^2 \text{ mol}^{-1}$	μ_B	selected IR $\text{abs}/\text{cm}^{-1}$			electronic spectra (solid state)/nm
				water	anion		
$\text{CoL}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	pink	65	4.94	3450	1050, 1120	447, 495, 540 (sh), 1000 (br)	
$\text{CoL}(\text{NCS})_2 \cdot 1/2 \text{H}_2\text{O}$	pink	33	4.89	3400	2075, 2055	495, 550 (sh), 620, 1080 (br)	
$\text{NiL}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	pale blue	68	3.07	3460	1120, 1055	365, 585, 700 (sh), 940 (br)	
NiLCl_2	pale blue	<i>b</i>	3.32			330 (sh), 600, 800 (sh), 1200 (br) ^c	
NiLBr_2	pale blue	<i>b</i>	3.23			~360 (sh), 605, ~750 (br), ~1200 (br) ^c	
$\text{NiL}(\text{NCS})_2 \cdot 1/2 \text{H}_2\text{O}$	lilac	33	3.19	3420	2080, 2060	360 (sh), 580, 940	
$\text{CuL}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	blue	67	1.84	3460	1120, 1045	575 (br) ^d	
$\text{CuLBr}_2 \cdot \text{H}_2\text{O}$	blue	41	1.94	3400		675 (br) ^d	

^a At $\sim 10^{-3} \text{ M}$ in dimethyl sulfoxide at 25 °C; expected range for a 1:1 electrolyte: 23–42 $\text{S cm}^2 \text{ mol}^{-1}$ (see: Geary, W. J. *Coord. Chem. Rev.* 1971, 7, 81). ^b Complex not sufficiently soluble to determine conductance. ^c Spectral peaks poorly resolved. ^d A very broad envelope of bands; these spectra also contain the edge of an intense band (possibly of charge-transfer nature) extending from the UV into visible region.

ion. The thiocyanate complexes each show (two) stretching modes near 2070 cm^{-1} in accord with these groups being N bound to the central metal.²⁰

The complex $\text{CoL}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ is a 2:1 electrolyte in methanol ($\Lambda = 160 \text{ S cm}^2 \text{ mol}^{-1}$; 25 °C) whereas the low solubilities of the other complexes precluded the measurement of their conductances in this solvent. However, in dimethyl sulfoxide each of the perchlorate complexes was found to be a 2:1 electrolyte (Table II) whereas the other complexes (where soluble) yielded values in the range corresponding to 1:1 electrolytes, indicating that substantial ionization of these complexes occurs in this donor solvent.

The visible near-infrared spectra of the complexes have been determined (Table II). Both cobalt(II) complexes exhibit

spectra which are typical of six-coordinate geometries, and both have magnetic moments within the range 4.7–5.2 μ_B which is characteristic of such a geometry. Similarly the spectra of the nickel complexes are typical of octahedral or pseudooctahedral nickel(II); the simple three-band spectrum of $\text{NiL}(\text{NCS})_2 \cdot 1/2 \text{H}_2\text{O}$ can readily be assigned to arise from the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F}) (\nu_1)$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F}) (\nu_2)$, and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P}) (\nu_3)$ transitions in O_h symmetry. The spectrum of each copper complex consists of a symmetrical envelope of bands which spans the visible region. Because of the broadness of the spectra, it is not possible to make reliable assignments for these complexes.

Spectrophotometric titrations of cobalt, nickel, and copper perchlorates in dimethyl sulfoxide with 3 have been carried out. Since this ligand contains eight potential donor atoms, the prospect of incorporating two metal ions in the macrocycle (each with an O_2N_2 -donor set) appeared possible especially

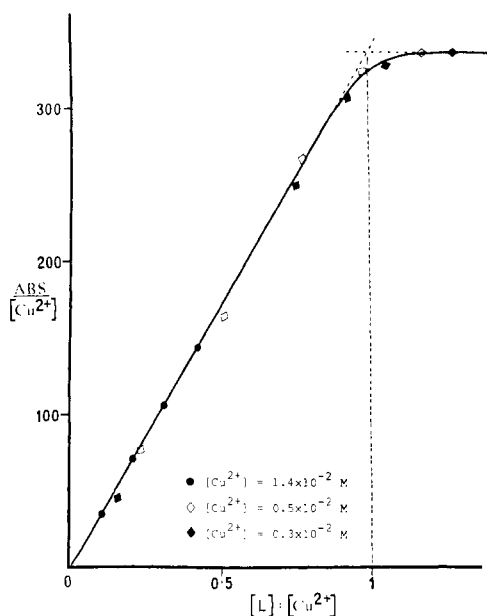


Figure 1. Spectrophotometric titration (at 605 nm) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in dimethyl sulfoxide with ligand 3.

since 1:1 complexes with these metal ions and O₂N₂-donor macrocycles of type 1 readily form.^{3,7,8} Although the scope of the titrations were limited somewhat by the low solubilities of the respective complexes, in no case was evidence obtained for the formation of a 2:1 species; the results for copper are given in Figure 1. It also appears significant that only 1:1 complexes were isolated from the synthetic studies. The observed 1:1 complexation very likely reflects the tendency of the respective metal ions to prefer the N₄-donor set of the macrocyclic ring since such an arrangement would be expected to result in enhanced thermodynamic stabilities with the metal ions used in the study. Thus, from the evidence presented so far, it seems very likely that some (or all) of the ether-oxygen atoms of the macrocycle do not coordinate in the respective complexes. Indeed, previous X-ray studies^{8,9} of metal complexes of a number of oxygen-nitrogen donor macrocycles show that ether groups of such macrocycles remain uncoordinated in the solid complexes; for example, the complex $[\text{CuL}(\text{H}_2\text{O})](\text{ClO}_4)_2$ ($L = 2$; $n = 2$, $m = 3$) has recently been shown to have a pseudo-square-planar geometry in which the donor atoms are the three nitrogen atoms of the macrocycle together with an oxygen from the water molecule.⁹ Further, physical measurements on the high-spin nickel(II) and low-spin cobalt(II) complexes of a 30-membered Schiff base macrocycle (incorporating an O₄N₆ heteroatom set) suggest that N₆-coordination spheres occur in the 1:1 (M:L) complexes of each of these ions.²¹

log K Determinations. So that further insight into the metal ion binding of 3 in solution could be obtained, the thermodynamic stabilities of the cobalt(II) and nickel(II) complexes of this ligand have been obtained potentiometrically (the copper(II) complex was not sufficiently soluble for a similar study).

The protonation constants K_1 – K_4 for 3 were determined in 95% methanol ($I = 0.1$, $(\text{CH}_3)_4\text{NCl}$) under conditions identical with those used in earlier studies.^{6–9} The following values were obtained: $K_1 = 9.66 \pm 0.01$, $K_2 = 8.20 \pm 0.02$, $K_3 = 6.03 \pm 0.01$, and $K_4 = 5.93 \pm 0.01$, where $K_1 = [\text{HL}^+]/[\text{L}][\text{H}^+]$, $K_2 = [\text{H}_2\text{L}^{2+}]/[\text{HL}^+][\text{H}^+]$, etc. The values are readily rationalized in terms of the expected electrostatic repulsions between

Table III. log Stability Constants for Cobalt(II) and Nickel (II) Complexes of Oxygen-Nitrogen Donor Macrocycles in 95% Methanol at 25 °C [$I = 0.1$, $(\text{CH}_3)_4\text{NCl}$]

ligand	donor set	log K^a		ref
		Co ²⁺	Ni ²⁺	
L = 1 ($n = m = 2$)	O ₂ N ₂		3.7	6
L = 1 ($n = 2$, $m = 3$)	O ₂ N ₂	<4.5	5.4	6, 8
L = 2 ($n = m = 2$)	O ₂ N ₃	$7.55 \pm 0.04^{b,c}$	9.96 ± 0.09	9
L = 2 ($n = 2$, $m = 3$)	O ₂ N ₃	7.27 ± 0.06	9.83 ± 0.06	9
L = 3	O ₄ N ₄	10.13 ± 0.10	12.61 ± 0.09	d

^a log K for the reaction $\text{M}^{2+} + \text{L} \rightleftharpoons \text{ML}^{2+}$. ^b Errors are 1 standard deviation. ^c Runs (three determinations) for this ligand with $\text{L}:\text{M}^{2+} = 2$ also gave evidence for the formation of a ML_2^{2+} species with $\log \beta_{\text{ML}_2} = 13.07 \pm 0.09$. ^d This work.

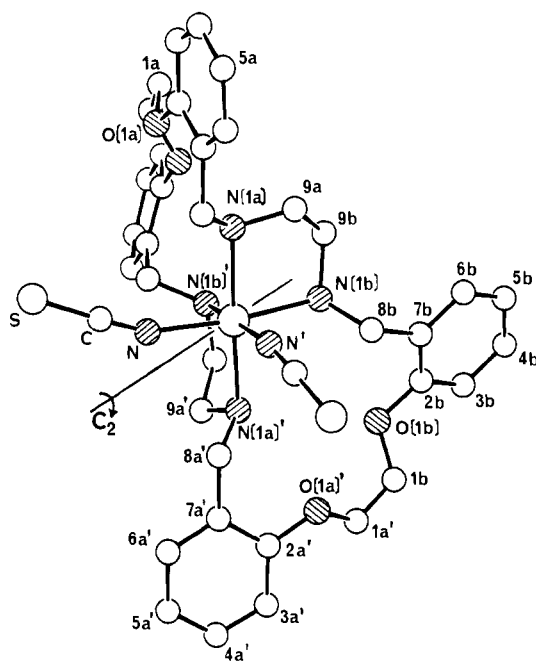


Figure 2. The complex $[\text{NiL}(\text{NCS})_2]$, $L = 3$, with atom labels as used in Tables I, IV, and V.

individual quaternary protons. Ionization of the first and second protons is expected to occur more readily than the remaining two because each of the former is separated from another protonation site by only a two-carbon bridge. The remaining sites are much more separated and hence give rise to higher log K values.

The stability constants for the complexes of 3 obtained during the present study are listed in Table III together with values for the corresponding complexes of the O₂N₂ macrocycles of type 1 and O₂N₃ macrocycles of type 2 determined previously under identical conditions.^{6,9} For the latter complexes, chemical and X-ray studies have demonstrated that all nitrogens of the respective ligands act as donors. The participation of an extra nitrogen in the complexes of 2 (relative to the complexes of 1) is clearly reflected by the increase in their respective log K values (Table III). Similarly, if the four nitrogen atoms of 3 coordinate to these metal ions as predicted above, then a further increase in the log K values is expected for these complexes and the values obtained clearly show (Table III) such a trend. For this latter system, precipitation of complex during the titration prevented the collection of a full set of data in each case; however, there was no evidence for the formation of other metal-containing species apart from the respective 1:1 complexes over the range of \bar{n} values used for the calculations (Ni, $\bar{n} = 0.02$ – 0.30 ; Co, $\bar{n} = 0.02$ – 0.90). It is especially significant, in view of the previous

(21) Nelson, S. M.; McCann, M.; Stevenson, C.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* 1979, 1477.

Table IV. Interatomic Bond Lengths and Angles for for $[\text{NiL}(\text{NCS})_2]\cdot\text{DMF}$

Bond Lengths/Å			
Ni-N(1a)	2.140 (5)	Ni-N(1b)	2.157 (6)
Ni-N	2.058 (6)	N-C	1.137 (8)
C-S	1.631 (8)	C(1a)-C(1b)	1.48 (1)
C(1a)-O(1a)	1.34 (1)	C(1b)-O(1b)	1.34 (1)
O(1a)-C(2a)	1.37 (1)	O(1b)-C(2b)	1.39 (1)
C(2a)-C(3a)	1.42 (1)	C(2b)-C(3b)	1.39 (1)
C(3a)-C(4a)	1.35 (1)	C(3b)-C(4b)	1.36 (1)
C(4a)-C(5a)	1.34 (1)	C(4b)-C(5b)	1.37 (1)
C(5a)-C(6a)	1.38 (1)	C(5b)-C(6b)	1.40 (1)
C(6a)-C(7a)	1.38 (1)	C(6b)-C(7b)	1.38 (1)
C(7a)-C(2a)	1.37 (1)	C(7b)-C(2b)	1.38 (1)
C(7a)-C(8a)	1.514 (9)	C(7b)-C(8b)	1.517 (9)
C(8a)-N(1a)	1.463 (8)	C(8b)-N(1b)	1.496 (8)
N(1a)-C(9a)	1.478 (9)	N(1b)-C(9b)	1.490 (9)
N(1a)-H(N1a)	0.84 (6)	N(1b)-H(N1b)	0.79 (6)
C(9a)-C(9b)	1.47 (1)	O(1s)-C(3s)	1.33 (4)
C(3s)-N(1s)	1.19 (5)	N(1s)-C(2s)	1.72 (6)
C(1s)-N(1s)	1.42 (6)		
Bond Angles/Deg			
N-Ni-N(1a)	92.0 (2)	N-Ni-N(1b)	173.1 (2)
N-Ni-N(1a)'	90.3 (2)	N-Ni-N(1b)'	89.6 (2)
N(1a)-Ni-N(1b)	82.5 (2)	N-Ni-N'	94.6 (2)
N(1a)-Ni-N(1a)'	176.6 (2)	N(1b)-Ni-N(1b)'	86.9 (2)
N(1a)'-Ni-N(1b)	95.0 (2)	Ni-N-C	158.4 (6)
N-C-S	178.3 (7)		
C(1b)-C(1a)-O(1a)	114 (2)	C(1a)-C(1b)-O(1b)	115 (2)
C(1a)-O(1a)-C(2a)	115 (1)	C(1b)-O(1b)-C(2b)	113 (1)
O(1a)-C(2a)-C(3a)	124.4 (9)	O(1b)-C(2b)-C(3b)	120.6 (8)
O(1a)-C(2a)-C(7a)	114.7 (7)	O(1b)-C(2b)-C(7b)	117.2 (7)
C(3a)-C(2a)-C(7a)	121.0 (9)	C(3b)-C(2b)-C(7b)	122.2 (2)
C(2a)-C(3a)-C(4a)	118 (1)	C(2b)-C(3b)-C(4b)	119.9 (9)
C(3a)-C(4a)-C(5a)	122 (1)	C(3b)-C(4b)-C(5b)	118.9 (9)
C(4a)-C(5a)-C(6a)	119 (1)	C(4b)-C(5b)-C(6b)	121.4 (9)
C(5a)-C(6a)-C(7a)	122 (1)	C(5b)-C(6b)-C(7b)	120.3 (9)
C(6a)-C(7a)-C(8a)	120.6 (8)	C(6b)-C(7b)-C(8b)	122.2 (7)
C(6a)-C(7a)-C(2a)	117.1 (8)	C(6b)-C(7b)-C(2b)	117.4 (8)
C(2a)-C(7a)-C(8a)	122.2 (7)	C(2b)-C(7b)-C(8b)	120.3 (7)
C(7a)-C(8a)-N(1a)	116.4 (6)	C(7b)-C(8b)-N(1b)	111.3 (6)
C(8a)-N(1a)-Ni	115.1 (4)	C(8b)-N(1b)-Ni	118.8 (5)
C(8a)-N(1a)-C(9a)	111.7 (6)	C(8b)-N(1b)-C(9b)	114.0 (6)
C(9a)-N(1a)-Ni	105.6 (4)	C(9b)-N(1b)-Ni	105.9 (4)
H(N1a)-N(1a)-Ni	106 (5)	H(N1b)-N(1b)-Ni	107 (5)
H(N1a)-N(1a)-C(8a)	115 (5)	H(N1b)-N(1b)-C(8b)	102 (5)
H(N1a)-N(1a)-C(9a)	103 (5)	H(N1b)-N(1b)-C(9b)	109 (5)
N(1a)-C(9a)-C(9b)	109.4 (7)	N(1b)-C(9b)-C(9a)	110.4 (7)

discussion, that M_2L^{4+} species were rejected when included in the equilibria to be processed by MINQUAD.¹² The greater stabilities of the respective nickel complexes relative to the corresponding cobalt complexes (Table III) is in accord with the expected Irving-Williams order.²²

X-ray Diffraction Study. So that fine details of its coordination geometry in the solid state could be investigated, the X-ray structure of $[\text{NiL}(\text{NCS})_2]\cdot\text{DMF}$ was determined. The structure confirms that the ether oxygen atoms are not coordinated and that the nickel ion has an approximately octahedral geometry, defined by the four nitrogen atoms of the macrocycle and two cis thiocyanate ions (see Figure 2). The nickel atom lies on a crystallographic twofold axis which passes through the midpoint between the cis thiocyanate nitrogen atoms. The macrocycle is folded about a line through N(1a) and N(1a)', giving the β -cis-type configuration which has been observed previously²³ for a number of quadridentate N_4 macrocycles with much smaller rings. The β -cis arrangement in $[\text{NiL}(\text{NCS})_2]$ requires the ligand **3** to define two unusually large (13-membered) chelate rings which span cis coordination sites. In these 13-membered rings, the atoms most remote

Table V. Shortest Intermolecular Contacts^a and Selected Intramolecular Contacts (<2.9 Å)

atoms ^b	dist/Å	atoms	dist/Å
O(1s)⋯H(N1b) ^I	2.34	C⋯H(6b) ^{IV}	2.82
O(1a)⋯H(N1a)	2.44	O(1a)⋯H(3b) ^{II}	2.82
O(1s)⋯H(9b1) ^{II}	2.54	S⋯H(5a) ^V	2.86
O(1b)⋯H(N1a) ^{III}	2.66	C(4a)⋯H(4b) ^{VI}	2.89

^a Excluding hydrogen-hydrogen contacts. ^b Positional parameters of the second atoms listed are related to those given in Table I by the following operations: (I) $x - 1/2, 1/2 + y, 1/2 - z$; (II) $1/2 + x, y - 1/2, 1/2 - z$; (III) $-x, y, 1/2 - z$; (IV) $x, 1 - y, 1/2 + z$; (V) $1/2 - x, 1/2 - y, 1/2 + z$; (VI) $1/2 + x, 3/2 - y, -z$.

from the nickel ion have high thermal parameters (see Table I). The ethane bridge -C(1a)-C(1b)- shows signs of disorder, but this could not be resolved into a suitable model to allow refinement with partial occupancies of different conformations (see Experimental Section). For the two crystallographically independent quarters of this ligand in the asymmetric unit (labeled *a* and *b* in Figure 2) the agreement is good between chemically equivalent bond lengths and angles (Table IV), and values are similar to those found^{4,6-8} in complexes of the related "monomer" ligand **1**.

The Ni-N(1a) and Ni-N(1b) lengths (see Table IV) fall toward the upper end of the range of values (2.04–2.16 Å) reported²⁴ for coordinate bonds from neutral sp^3 -hybridized nitrogen atoms in high-spin nickel(II) complexes of quadridentate macrocycles with 14-, 15-, and 16-membered rings.

Evidence for hydrogen-bonding involving the secondary amine groups is equivocal. The hydrogen atom H(N1a) has two very weak intermolecular contacts with the ether oxygen atoms O(1a) and O(1b) (see Table V). The dimethylformamide oxygen O(1s), which lies on the twofold axis, interacts weakly with N(1b) and N(1b)'. There are no other significant intermolecular contacts.

The structure determination demonstrates that the macrocycle **3** is capable of providing an N_4 -donor set without incorporation of unfavorable strain in the backbone of the ligand. There are no structural features which would prevent the ligand behaving as a dinucleating system (providing both metal ions with an O_2N_2 -donor set), but clearly the preference shown by cobalt(II), nickel(II), and copper(II) for amine over ether donor atoms results in the mononuclear complexes (Table II) being more stable. Related ligands in which the phenoxy groups have been replaced by anilino groups have been shown^{18,25} to be capable of incorporating two metal ions.

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Registry No. **3**, 78891-75-5; $[\text{NiL}(\text{NCS})_2]\cdot\text{DMF}$, 78891-60-8; $\text{CoL}(\text{ClO}_4)_2$, 78891-58-4; $\text{CoL}(\text{NCS})_2$, 78891-57-3; $\text{NiL}(\text{ClO}_4)_2$,

(22) Irving, H.; Williams, R. J. P. *J. Chem. Soc.* **1953**, 3192.

(23) Curtis, N. F. In "Co-ordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter 4.

(24) For eight structures of high-spin nickel(II) complexes with 14- to 16-membered macrocyclic ligands, retrieved from the Cambridge Crystallographic Data Centre files using the "Crystal Structure Search Retrieval" program (M. Elder, P. Machin, and O. S. Mills, SRC Daresbury Laboratory, Warrington, WA4 4AD, U.K., 1977).

(25) Dancey, K. P.; Tasker, P. A.; Price, R.; Hatfield, W. E.; Brower, D. C. *J. Chem. Soc., Chem. Commun.* **1980**, 1248.

78891-56-2; NiLCl₂, 78891-55-1; NiLBr₂, 78891-54-0; NiL(NCS)₂, 78891-59-5; CuL(ClO₄)₂, 78891-53-9; CuLBr₂, 78891-52-8; 1,4-bis(2-formylphenyl)-1,4-dioxabutane, 52118-10-2; ethane-1,2-diamine, 107-15-3.

Supplementary Material Available: Listings of analytical data for the complexes (Table S1) and structure factors (Table S2) for the nickel complex (12 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structures of the Hexafluoroarsenate and Hexafluoroantimonate Salts of the Dimeric Thiodiselenazyl Cation Se₄S₂N₄²⁺

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The reactions of S₄N₄ with Se₄(AsF₆)₂, Se₄(Sb₂F₁₁)₂, and Se₈(AsF₆)₂ in SO₂ have been found to give the first well-characterized examples of a sulfur-selenium-nitrogen cationic ring in the compounds (Se₄S₂N₄)(AsF₆)₂ and (Se₄S₂N₄)(SbF₆)₂. Blue-green crystals of both compounds are isomorphous and crystallize in the monoclinic space group P2₁/n. The cell dimensions of the hexafluoroarsenate salt determined at -30 °C are *a* = 10.358 (3) Å, *b* = 16.002 (5) Å, *c* = 9.748 (4) Å, and β = 98.16 (3)°; those of the hexafluoroantimonate salt, determined at 22 °C, are *a* = 10.619 (1) Å, *b* = 16.523 (2) Å, *c* = 9.873 (2) Å, and β = 97.70 (1)°. In both salts, the bis(thiodiselenazyl) cation, Se₄S₂N₄²⁺, is very similar to the bis(thiodithiazyl) cation in that it consists of two thiodiselenazyl rings linked by long Se...Se interactions of 3.12-3.18 Å between the diselenide bonds in each ring. The cation also has some significant interactions with the hexafluoroarsenate and hexafluoroantimonate anions. These cation-cation and anion-cation interactions are discussed and compared to similar interactions in the sulfur-nitrogen cations and other selenium compounds.

Introduction

The synthesis of the monomeric and dimeric forms of the thiodithiazyl cation, S₃N₂⁺ and S₆N₄²⁺, by the oxidation of S₄N₄ with Te₆⁴⁺ and S₈²⁺, respectively, has been reported recently.¹ These novel oxidations raised the question as to whether the analogous reactions of S₄N₄ with the selenium cations Se₄²⁺ and Se₈²⁺ would also give a sulfur-nitrogen cation or alternatively a mixed sulfur-selenium-nitrogen cation, no example of which had been well characterized. The first report of a compound possibly containing a S-Se-N cation was made by Garcia-Fernandez,² who obtained a compound, which was reported to analyze as SeS₂N₂Cl₅, from the reaction of selenium dichloride and S₄N₄ in thionyl chloride. However, Bannister and co-workers³ were unable to reproduce these results, and they suggested that the compound was probably Se₂S₄N₄Cl₂ for which some possible structures were postulated. Recently Street and co-workers⁴ have reported the preparation of compounds formulated as (S₂Se₄N₄²⁺)(Cl⁻)₂ and (S₂Se₄N₄²⁺)(Br⁻)₂ from the reactions of bis[tris(trimethylsilyl)amino]sulfane and the appropriate selenium tetrahalide in methylene chloride. On the basis of infrared and mass spectroscopic data and the absence of an ESR signal from the solid compounds the structures of these new cations were proposed to be analogous to that of the S₆N₄²⁺ cation as determined by Bannister et al.⁵ However, because of the insolubility of the compounds, no crystals could be obtained for a definite X-ray crystallographic confirmation of the proposed structures.

In this paper, we show that oxidation of S₄N₄ using either of the cations Se₄²⁺ and Se₈²⁺ gives the sulfur-selenium-ni-

trogen dimeric cation Se₄S₂N₄²⁺. The structure of this ion has been determined by an X-ray crystallographic study of its hexafluoroarsenate and hexafluoroantimonate salts.

Experimental Section

Reaction vessels, the recording of IR spectra, and the preparation of S₄N₄ were the same as described previously.¹ Salts of Se₄²⁺ and Se₈²⁺ were prepared with use of established methods^{6a} but with the following modifications.

Preparations of Se₈(AsF₆)₂. In a typical experiment 10.1 g (16 mmol of Se₈) of selenium powder (Alfa Inorganics) was used with the stoichiometric amount of AsF₅. The product was extracted near the freezing point of sulfur dioxide because of its increased solubility at low temperatures. The yield was 14.5 g (90% based on Se₈) of semicrystalline Se₈(AsF₆)₂.

Preparation of Se₄(AsF₆)₂ and Se₄(Sb₂F₁₁)₂. In typical experiments 3.0 g (38 mmol) of powdered selenium was used with 57 mmol of AsF₅ and 70 mmol of SbF₅. In the latter case approximately twice as much solvent (100 mL) was used to avoid formation of the SbF₅·SO₂ adduct.^{6b} The products were used without further purification.

Reaction of S₄N₄ with Se₈(AsF₆)₂ in SO₂. S₄N₄ (0.152 g, 0.83 mmol) and Se₈(AsF₆)₂ (0.833 g, 0.83 mmol) were transferred to separate sides of a double-bulb reaction vessel. The vessel was then evacuated, and sulfur dioxide (ca. 15 mL) condensed at -196 °C onto the solid reactants. Both sides of the apparatus were flame sealed. The mixture was allowed to warm slowly to room temperature and stirred for 24 h. A dark green solution was obtained initially, which slowly changed to a reddish-brown solution containing a black precipitate, which was identified as a Se/S mixture by XRF and powder diffraction data. After filtration at room temperature and very slow removal of the solvent, blue-green crystals, identified by crystallographic examination as Se₄S₂N₄(AsF₆)₂, were obtained (0.25 g, 0.31 mmol; 37% yield based on S₄N₄). In some preparations an unidentified orange-red powder was also obtained. On exposure to air the blue-green crystals quickly decompose to a brown solid, which further decomposes to an orange material. Infrared spectrum of Se₄S₂N₄(AsF₆)₂: 1304 (w), 1260 (vw), 1223 (w), 1165 (m), 1153 (m), 1091

(1) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.*, in press.
(2) Garcia-Fernandez, H. C. R. *Hebd. Seances Acad. Sci.* **1961**, 252, 411.
(3) Bannister, A. J.; Padley, J. S. *J. Chem. Soc. A* **1967**, 1437.
(4) Wolmershäuser, G.; Brulet, G. R.; Street, G. B. *Inorg. Chem.* **1978**, 17, 3586.
(5) Bannister, A. J.; Clarke, H. G.; Rayment, I. *Inorg. Nucl. Chem. Lett.* **1974**, 10, 647.

(6) (a) Gillespie, R. J.; Ummat, P. K.; Dean, P. A. W. *Inorg. Synth.* **1974**, 15, 215. (b) Dean, P. A. W.; Gillespie, R. J. *J. Am. Chem. Soc.* **1969**, 91, 7260.