

Jahn-Teller distortion with the axial bonds 0.139 Å longer than the equatorial. Also, the axial bonds are 0.01 Å longer than those of the Ni(9-aneN<sub>3</sub>)<sub>2</sub><sup>2+</sup>, whereas the equatorial bonds are 0.129 Å shorter in the Ni(III) species. The self-exchange rate constant for the bis(nonane) system ( $6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) is similar to that found in this study. For the *trans*-Ni(cyclam)Cl<sub>2</sub><sup>+0</sup> exchange ( $k = 3.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>35</sup> the corresponding changes are  $\Delta d(\text{Ni}-\text{Cl}) = 0.04 \text{ \AA}$  and  $\Delta d(\text{Ni}-\text{N}) = 0.088 \text{ \AA}$ . If the electron is removed from the  $d_{x^2-y^2}$  orbital, then contraction in the equatorial plane will be a factor, and the smaller changes in the dichloro complex may contribute to a more rapid exchange. Clearly, more data are required for a full analysis of these  $d^8/d^7$  reactions. However, methyls, which should hinder ligand rearrangement and perturb the cavity about the metal ion through H-H repulsions, make only slight differences in self-exchange rates. The imposition of greater structural rearrangement, possibly through the use of pendant-arm macrocycles,<sup>36</sup> may be required to provide the sort

of bond length difference discrimination and, hence, rate variations observed in other systems.<sup>26</sup> Studies are under way to investigate these aspects.

**Acknowledgment.** We thank the NSERC for financial support. C.X. is indebted to the People's Republic of China for a fellowship. It is a pleasure to acknowledge practical assistance from Dr. C. J. Macdonald.

**Registry No.** (R)-Me-9-ane, 112816-31-6; [Ni(Me-9-aneN<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 68011-41-6; Ni<sup>IV</sup>(oxime), 55188-33-5; Co(phen)<sub>3</sub><sup>2+</sup>, 16788-34-4; I<sub>2</sub>, 20461-54-5; Ni(9-ane N<sub>3</sub>)<sub>2</sub><sup>3+</sup>, 86709-81-1; Ni(cyclam)<sup>3+</sup>, 66199-97-1; (R)-NH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>NH<sub>2</sub>, 6852-78-4; (R)-TsNHCH(CH<sub>3</sub>)CH<sub>2</sub>NHTs, 112816-32-7; (R)-TsNCH(CH<sub>3</sub>)CH<sub>2</sub>NHTs, 112816-33-8; TsOCH<sub>2</sub>CH<sub>2</sub>N(Ts)CH<sub>2</sub>CH<sub>2</sub>OTs, 16695-22-0; (R)-TsNHCH<sub>2</sub>CH(CH<sub>3</sub>)N(Ts)CH<sub>2</sub>CH<sub>2</sub>N(Ts)CH<sub>2</sub>CH<sub>2</sub>OTs, 112816-34-9; NaH, 7646-69-7; (R)-TsNCH(CH<sub>3</sub>)CH<sub>2</sub>N(Ts)CH<sub>2</sub>CH<sub>2</sub>N(Ts)CH<sub>2</sub>CH<sub>2</sub>, 112816-35-0; [Ni(Me-9-aneN<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>, 112816-37-2.

**Supplementary Material Available:** Table I, listing rates of hydrolysis of Ni((-)-(R)-Me-9-aneN<sub>3</sub>)<sub>2</sub><sup>2+</sup> in acidic media, Table II, listing rate data for the reactions of Ni((-)-(R)-Me-9-aneN<sub>3</sub>)<sub>2</sub><sup>2+</sup> with Ni(9-aneN<sub>3</sub>)<sub>2</sub><sup>3+</sup> and Ni(cyclam)<sup>3+</sup>, and Figure 1, showing a plot of  $k_2$  versus  $[\text{H}^+]^{-1}$  for the reaction of Ni((-)-(R)-Me-9-aneN<sub>3</sub>)<sub>2</sub><sup>2+</sup> with Co<sup>3+</sup>(aq) (4 pages). Ordering information is given on any current masthead page.

(35) McAuley, A.; Olubuyide, O.; Spencer, L.; West, P. R. *Inorg. Chem.* **1984**, *23*, 2594.

(36) Van der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 3489.

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and Inorganic Chemistry Laboratory and Chemical Crystallography Laboratory, University of Oxford, Oxford OX1 3QR, United Kingdom

## Crown Thioether Chemistry: Homoleptic Hexakis(thioether) Complexes of Nickel(II)

Stephen R. Cooper,\* Simon C. Rawle, Judith Ann R. Hartman, Eric J. Hints, and Gary A. Admans

Received July 16, 1987

The Ni(II) complexes of 1,4,7,10,13,16-hexathiacyclooctadecane (18S6, hexathia-18-crown-6), 2,5,8-trithianonane, 1,5,9-trithiacyclododecane (12S3, trithia-12-crown-3), and 1,5,9,13,17,21-hexathiacyclotetradecane (24S6, hexathia-24-crown-6) have been synthesized and characterized by single-crystal X-ray diffraction and electronic spectroscopy. Each of these complexes contains a high-spin [Ni(thioether)<sub>6</sub>]<sup>2+</sup> cation with octahedral microsymmetry. Comparison of these complexes shows that within a conserved coordination sphere the different ring sizes (1) change the Ni-S distances by up to 0.05 Å, (2) affect the ligand field splitting by up to 10%, and (3) greatly influence the stability of the resulting complexes. Crystallographic data: [Ni(18S6)](picrate)<sub>2</sub>, C<sub>24</sub>H<sub>28</sub>N<sub>6</sub>O<sub>14</sub>S<sub>6</sub>Ni, monoclinic, space group C2/c (No. 15),  $a = 21.079$  (6) Å,  $b = 8.685$  (2) Å,  $c = 18.399$  (5) Å,  $\beta = 93.63$  (2)°,  $Z = 4$ ; [Ni(12S3)]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>, C<sub>18</sub>H<sub>36</sub>B<sub>2</sub>F<sub>8</sub>S<sub>6</sub>Ni, orthorhombic, space group Pbcn (No. 61),  $a = 19.369$  (9) Å,  $b = 12.500$  (5) Å,  $c = 11.862$  (2) Å,  $Z = 4$ ; [Ni(24S6)](BF<sub>4</sub>)<sub>2</sub>, C<sub>18</sub>H<sub>36</sub>B<sub>2</sub>F<sub>8</sub>S<sub>6</sub>Ni, monoclinic, space group C2/c (No. 15),  $a = 13.744$  (5) Å,  $b = 17.021$  (5) Å,  $c = 13.801$  (5) Å,  $\beta = 113.25$  (3)°,  $Z = 4$ .

### Introduction

The electronic consequences of thioether coordination has been a recurring theme in research on the blue copper proteins. Such consequences are best assessed in the context of a homoleptic thioether coordination sphere. Until recently, however, few homoleptic thioether complexes were known; simple dialkyl thioethers often do not bind strongly enough to yield isolable tetrakis- or hexakis(thioether) complexes.<sup>1</sup>

Crown thioethers provide a general solution to this problem. Recent synthetic improvements<sup>2,3</sup> have made readily available a range of ligands (Figure 1)<sup>4</sup> capable of enforcing hexakis(thioether) coordination. Accordingly, their use has recently yielded the first examples of hexakis(thioether) complexes of a number of transition metal ions.<sup>5</sup>

Recent work has also shown that in many cases crown thioether coordination confers unusual electronic structures on a transition-metal ion.<sup>5</sup> For example, [Rh(9S3)]<sub>2</sub><sup>3+</sup> undergoes reduction to the Rh(I) complex by way of a rare example of a monomeric Rh(II) species.<sup>6,7</sup>

Such unusual behavior inevitably raises the question of whether it arises from the hexakis(thioether) coordination sphere or from

a specific effect of the crown ligand. It also raises another question: to what extent can molecular and electronic structure be tuned by geometric deformation of a conserved homoleptic coordination sphere? Ultimately this type of tuning may play a critical role in control of reactivity or specificity of catalytic action.

Several factors make Ni(II) an ideal choice for investigation of these issues. Historically Ni(II) has played a prominent role in the development of coordination chemistry. This is particularly true in the case of macrocyclic thioethers, first studied in the seminal work of Rosen and Busch<sup>8,9</sup> and of Black and McLean.<sup>10,11</sup>

- (1) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365-414.
- (2) Wolf, R. E., Jr.; Hartman, J. R.; Ochrymowicz, L. A.; Cooper, S. R.; *Inorg. Synth.* in press.
- (3) Blower, P. J.; Cooper, S. R. *Inorg. Chem.* **1987**, *26*, 2009.
- (4) Abbreviations used: 9S3, 1,4,7-trithiacyclononane (trithia-9-crown-3); 12S4, 1,4,7,10-tetrathiacyclododecane (tetrathia-12-crown-4); 14S4, 1,4,8,11-tetrathiacyclotetradecane (tetrathia-14-crown-4); 15S5, 1,4,7,10,13-pentathiacyclopentadecane (pentathia-15-crown-5); 18S6, 1,4,7,10,13,16-hexathiacyclooctadecane (hexathia-18-crown-6); 24S6, 1,5,9,13,17,21-hexathiacyclotetradecane (hexathia-24-crown-6); ttn, 2,5,8-trithianonane; pic, picrate.
- (5) Cooper, S. R. *Acc. Chem. Res.*, in press.
- (6) Rawle, S. C.; Yagbasan, R.; Prout, K.; Cooper, S. R.; *J. Am. Chem. Soc.* **1987**, *109*, 6181.
- (7) Rawle, S. C.; Yagbasan, R.; Cooper, S. R., manuscript in preparation.
- (8) Rosen, W.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 4694.

\* To whom correspondence should be addressed at the Inorganic Chemistry Laboratory, University of Oxford.

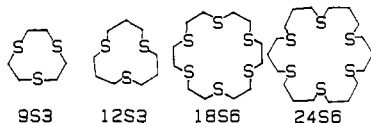


Figure 1. Ligands used in this work.<sup>4</sup>

Recently Glass et al.<sup>12</sup> have reported structural work on  $[\text{Ni}(\text{9S3})_2]^{2+}$ , while we have published preliminary structural investigations of  $[\text{Ni}(\text{18S6})]^{2+}$ <sup>13</sup> and  $[\text{Ni}(\text{24S6})]^{2+}$ .<sup>14</sup> The extensive data already available make Ni(II) complexes a convenient yardstick for evaluation and comparison of crown thioether ligands. In another source of interest, Kellogg and co-workers<sup>15</sup> have very recently described the use of Ni-crown thioether complexes in organic synthesis.

To gain further insight into the crown thioethers 12S3, 18S6, and 24S6 and to examine the magnitude of tuning they make available, we have investigated the Ni(II) complexes of these ligands by optical, magnetic, and structural methods. We report herein the results of that investigation.

### Experimental Section

Standard Schlenk and syringe techniques were used for preparation of complexes. Nickel hexakis(ethanol) tetrafluoroborate was prepared as described previously.<sup>16</sup> Electronic spectra were recorded in nitromethane solution on Cary 17 and Perkin-Elmer 552 spectrophotometers. Magnetic measurements in the solid state were performed on a Johnson Mathey magnetic balance and those in solution by the NMR method.<sup>17-20</sup>

1,4,7,10,13,16-Hexathia-18-crown-6 (18S6),<sup>2</sup> 1,4,7-trithiacyclononane (9S3),<sup>3</sup> 1,5,9-trithiacyclododecane (12S3),<sup>2</sup> and 1,5,9,13,17,21-hexathiacyclotetracosane (24S6)<sup>2</sup> were synthesized by published methods. Nickel(II) picrate, nickel(II) tetrafluoroborate, and nickel(II) trifluoroacetate were prepared from nickel(II) carbonate and the appropriate acid and then dried in vacuo over phosphorous pentoxide. Nitromethane and acetic anhydride were distilled from  $\text{P}_2\text{O}_5$  and stored over molecular sieves; acetonitrile and methylene chloride were freshly distilled from barium oxide. Diethyl ether was distilled from sodium benzophenone ketyl. All other chemicals were used as received. Nickel analysis was by EDTA titration.<sup>21</sup> Other analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or by M. Gascoyne, J. Kench, and A. Douglas of the Analytical Service of the Inorganic Chemistry Laboratory, Oxford, United Kingdom.

**Preparation of Compounds.**  $[\text{Ni}(\text{ttn}_2)](\text{BF}_4)_2$ . Nickel(II) tetrafluoroborate hexahydrate (152 mg, 0.446 mmol) was dissolved in 3 mL of 15% acetic anhydride in nitromethane to give a light green solution. After addition of 2,5,8-trithianonane (300 mg, 1.65 mmol), the resulting deep blue solution was concentrated to 1.4 mL and carefully covered with a layer of tetrahydrofuran. Within 24 h the solution deposited deep purple crystals that were collected by filtration, washed well with methylene chloride, and dried in vacuo overnight. Yield: 215 mg (80.9%). Anal. Calcd for  $\text{C}_{12}\text{H}_{28}\text{S}_6\text{NiB}_2\text{F}_8$ : C, 24.14; H, 4.74; S, 32.22. Found: C, 24.60; H, 4.83; S, 32.61. IR (Nujol,  $\text{cm}^{-1}$ ): 1562 (m), 1450 (s), 1440 (sh), 1430 (sh), 1335 (vw), 1308 (sh), 1288 (w), 1278 (sh), 1260 (w), 1100 (sh), 1055 (sh), 972 (m), 948 (w), 902 (w), 842 (w), 8768 (vw), 722 (w), 655 (w), 645 (w), 618 (vw), 518 (m). Recrystallization from tetrahydrofuran/nitromethane gave purple needles suitable for X-ray diffraction.

$[\text{Ni}(\text{18S6})](\text{pic})_2$ . A solution of 18S6 (10 mg, 0.03 mmol) in 5 mL

of acetone was added to a refluxing solution of nickel(II) picrate (15 mg, 0.03 mmol) in 5 mL of acetone. The resulting bright yellow solution was refluxed for 20 min and then allowed to cool to room temperature. The orange crystalline product was collected by filtration, washed with acetone, and dried in vacuo overnight. Yield: 19 mg (80%). Anal. Calcd for  $\text{C}_{24}\text{H}_{28}\text{N}_6\text{O}_4\text{S}_6\text{Ni}$ : C, 32.92; H, 3.23; N, 9.60; S, 21.97. Found: C, 32.74; H, 3.46; N, 9.36; S, 21.91. Recrystallization from hot acetonitrile afforded beautiful orange monoclinic prisms suitable for X-ray diffraction studies.

$[\text{Ni}(\text{18S6})](\text{CF}_3\text{CO}_2)_2 \cdot (\text{CF}_3\text{CO})_2\text{O}$ . Nickel(II) trifluoroacetate (260 mg, 0.91 mmol) was dissolved in 15 mL of 5% trifluoroacetic anhydride in nitromethane. Hexathia-18-crown-6 (205 mg, 0.568 mmol) was added, and the purple mixture was refluxed for 6 h, concentrated to 5 mL, and cooled to 5 °C. The resulting pink needles were collected by filtration, washed with cold nitromethane, and dried in vacuo overnight. Yield: 220 mg (60.6%). (Additional product could be recovered by concentrating the supernatant further.) Anal. Calcd for  $\text{C}_{20}\text{H}_{24}\text{S}_6\text{O}_7\text{F}_{12}\text{Ni}$ : C, 28.08; H, 2.83; S, 22.49; Ni, 6.86. Found: C, 27.42; H, 2.97; S, 22.20; Ni, 6.87. IR (Nujol,  $\text{cm}^{-1}$ ): 1784 (s, br), 1450 (m), 1300 (vw), 1200 (s, br), 1180 (sh), 1135 (s, br), 1008 (vw), 975 (vw), 949 (m), 812 (m), 788 (m), 706 (m), 607 (w), 512 (w), 425 (w). Solutions of this material dissolved in nitromethane containing a trace of trifluoroacetic anhydride were used for spectroscopic studies.

$[\text{Ni}(\text{12S3})_2](\text{BF}_4)_2$  was made by addition of trithia-12-crown-3 (88 mg, 0.4 mmol) to a solution of  $[\text{Ni}(\text{EtOH})_6](\text{BF}_4)_2$  (102 mg, 0.2 mmol) in acetic anhydride (5 mL) to give a deep blue solution. Vapor diffusion with diethyl ether gave the product as blue plates. Anal. Calcd for  $\text{C}_{18}\text{H}_{36}\text{S}_6\text{B}_2\text{F}_8\text{Ni}$ : C, 31.9; H, 5.32; Ni, 8.67. Found: C, 32.0; H, 5.35; Ni, 8.59.

$[\text{Ni}(\text{24S6})](\text{BF}_4)_2$ . To a solution of nickel(II) hexakis(ethanol) tetrafluoroborate (51 mg, 0.1 mmol) in acetic anhydride (3 mL) under nitrogen was added 24S6 (44 mg, 0.1 mmol) to give a deep blue-green solution. Vapor diffusion of hexane into a solution of  $[\text{Ni}(\text{24S6})](\text{BF}_4)_2$  in dichloromethane gave diffraction-quality crystals as turquoise needles. Anal. Calcd for  $\text{C}_{18}\text{H}_{36}\text{S}_6\text{B}_2\text{F}_8\text{Ni}$ : C, 31.9; H, 5.32; Ni, 8.67. Found: C, 32.0; H, 5.60; Ni, 8.57.

Solution magnetic susceptibility studies in  $\text{CH}_3\text{NO}_2$  on  $[\text{Ni}(\text{18S6})](\text{CF}_3\text{CO}_2)_2$  and  $[\text{Ni}(\text{ttn}_2)](\text{BF}_4)_2$  confirm that both complexes are high-spin ( $\mu_{298} = 2.77\mu_B$  ( $\chi_M = 3.24 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ ) and  $\mu_{298} = 2.80\mu_B$  ( $\chi_M = 3.31 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ ), respectively). The close similarity in optical spectra of all of the  $[\text{Ni}(\text{SR}_2)_6]^{2+}$  complexes indicates that all of them contain high-spin Ni(II).

**X-ray Crystallography. General Procedures.** A suitable single crystal was sealed in a quartz capillary and centered on an Enraf-Nonius CAD4 or Syntex R3 automatic diffractometer that generated  $\text{Mo K}\alpha$  (0.71069 Å) radiation (graphite monochromator). An orientation matrix was determined by least-squares fitting of the setting angles of at least 20 reflections well distributed in reciprocal space. During collection of the data set three standard reflections were measured every hour, but in no case was appreciable (>2%) decay evident. An empirical absorption correction was applied. After data reduction (including correction for Lorentz and polarization effects and averaging of equivalent reflections) the remaining unique reflections with  $I > 2$  (or  $3\sigma(I)$ ) were used for subsequent structure solution and refinement. Calculations were performed either on a VAX 11/750 computer with the CRYSTALS suite of crystallographic programs or on a Nova computer with the SHELXTL program. Positions for the Ni atoms (and in some cases, S atoms) were deduced from sharpened three-dimensional Patterson maps. A Fourier map phased by the Ni atoms showed most of the remaining non-hydrogen atoms. Full-matrix (for  $[\text{Ni}(\text{12S3})_2]^{2+}$  and  $[\text{Ni}(\text{24S4})]^{2+}$ ) or block-cascade (for  $[\text{Ni}(\text{18S6})]^{2+}$ ) least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms was continued to convergence. Most of the H atoms were located by Fourier difference syntheses, though all were included in calculated positions and a group isotropic thermal parameter was refined. Specific details for each of the structures appear in Table I.

**X-ray Diffraction Data Collection.**  $[\text{Ni}(\text{18S6})](\text{pic})_2$ . Systematic absences ( $hkl$ ,  $h + k$  odd;  $h0l$ ,  $l$  odd) indicated space group  $Cc$  or  $C2/c$ ; subsequent refinement showed the latter to be correct. The structure was solved with use of 2582 unique reflections with  $I > 2\sigma(I)$ . The hydrogen atoms were located and included as fixed atoms with isotropic thermal parameters set to six-fifths that of the bound carbon. Block-cascade least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms gave final agreement factors of  $R = 5.09$  and  $R_w = 5.48$  for 232 variables. The highest peak in the final difference Fourier map had an electron density of  $0.41 \text{ e } \text{Å}^{-3}$  and was located near the metal atom.

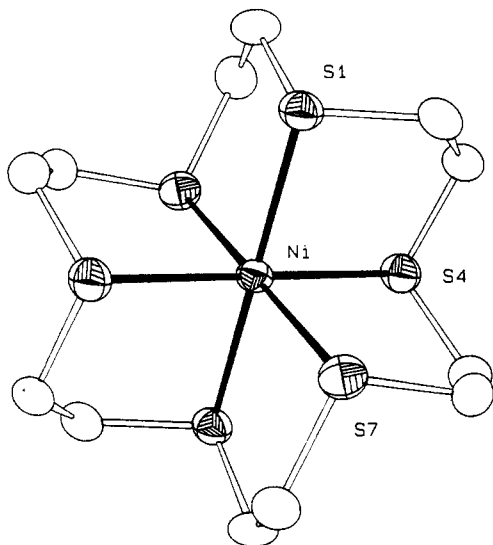
$[\text{Ni}(\text{12S3})_2](\text{BF}_4)_2$  gave systematic absences uniquely consistent with space group  $Pbca$ . The structure was solved with use of 1449 unique reflections with  $I > 2\sigma(I)$ . Approximately half of the hydrogen atoms

- (9) Rosen, W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 262.
- (10) Black, D. St. C.; McLean, I. A. *Tetrahedron Lett.* **1969**, 3961.
- (11) Black, D. St. C.; McLean, I. A. *Aust. J. Chem.* **1971**, *24*, 1401.
- (12) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.
- (13) Hintsa, E. J.; Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 3738.
- (14) Rawle, S. C.; Hartman, J. R.; Watkin, D. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1986, 1083.
- (15) Vriessma, B. K.; Lemaire, M.; Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1986**, *51*, 5169.
- (16) Van Leeuwen, P. W. N. M. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 247.
- (17) Reilly, C. A.; McConnell, H. M.; Meisenheimer, R. G. *Phys. Rev.* **1955**, *98*, 264.
- (18) Klein, M. P.; Holder, B. E. *Phys. Rev.* **1955**, *98*, 265.
- (19) Evans, D. F. *J. Chem. Soc.* **1959**, 2003-5.
- (20) Bartle, K. D.; Jones, D. W.; Maricic, S. *Croat. Chem. Acta* **1968**, *40*, 227-40.
- (21) Vogel, A. I. *Quantitative Inorganic Analysis*, 3rd ed.; Longman, London, 1961; p 435.

**Table I.** Crystallographic Data for [Ni(18S6)](pic)<sub>2</sub>, [Ni(12S3)]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>, and [Ni(24S6)](BF<sub>4</sub>)<sub>2</sub>

	[Ni(18S6)]-(pic) <sub>2</sub>	[Ni(12S3)] <sub>2</sub> -(BF <sub>4</sub> ) <sub>2</sub>	[Ni(24S6)]-(BF <sub>4</sub> ) <sub>2</sub>
formula	C <sub>24</sub> H <sub>28</sub> N <sub>6</sub> O <sub>4</sub> S <sub>6</sub> Ni	C <sub>18</sub> H <sub>36</sub> S <sub>6</sub> NiB <sub>2</sub> F <sub>8</sub>	C <sub>18</sub> H <sub>36</sub> S <sub>6</sub> NiB <sub>2</sub> F <sub>8</sub>
mol wt	875.65	677.22	677.22
system	monoclinic	orthorhombic	monoclinic
space group	C2/c (No. 15)	Pbca (No. 61)	C2/c (No. 15)
a, Å	21.079 (6)	19.369 (9)	13.744 (5)
b, Å	8.685 (2)	12.500 (5)	17.021 (5)
c, Å	18.399 (5)	11.862 (2)	13.801 (5)
α, deg	90	90	90
β, deg	93.63 (2)	90	113.25 (3)
γ, deg	90	90	90
vol, Å <sup>3</sup>	3361.5	2872.1	2966.3
d <sub>calc</sub> , g/cm <sup>3</sup>	1.73	1.57	1.52
Z	4	4	4
λ	Mo Kα	Mo Kα	Mo Kα
F(000)	1799.7	1400	1400
μ, cm <sup>-1</sup>	10.10	11.2	11.2
cryst size, mm	0.25 × 0.37 × 0.32	0.7 × 0.7 × 0.7	0.28 × 0.28 × 0.34
reflens collcd	+h,+k,±l	+h,+k,+l	+h,+k,±l
no. of reflens collcd	5852	4362	6375
no. of unique data with F <sup>2</sup> > 3σ(F <sup>2</sup> )	2582	1449	2370
2θ range, deg	3–60	3–52	3–54
final R, %	5.09	4.77	4.81
final R <sub>w</sub> , %	5.48	5.84	5.69
GOF <sup>a</sup>	1.076	1.24	1.08
no. of variables	232	153	189
temp	ambient	ambient	ambient
scan rate	2.00–29.3	4.8–1.6	0.7–3.7
mode	θ–2θ	ω–2θ	ω–2θ
R <sub>merg</sub>	0.0158	0.0182	0.0144

<sup>a</sup>The goodness of fit is defined as  $[\sum w(|F_o| - |F_c|)^2 / (n_o - n_v)]^{1/2}$ , where  $n_o$  and  $n_v$  denote the number of data and variables, respectively.



**Figure 2.** ORTEP drawing of the [Ni(18S6)]<sup>2+</sup> cation showing thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity). Numbering of unique atoms follows the IUPAC convention; i.e., atoms are numbered sequentially around ring (S1, C2, etc.)

were located; all were included in calculated positions and assigned a group isotropic thermal parameter, which was refined. Least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms gave final agreement factors of  $R = 4.77$  and  $R_w = 5.84$  for 153 variables. Attempts to model the positional disorder of the C5–C6–C7 part of the ring were unsuccessful; accordingly, distances involving these atoms are unreliable. The highest peak in the final difference Fourier map had an electron density of  $0.4 \text{ e } \text{Å}^{-3}$  and was located near C6.

[Ni(24S6)](BF<sub>4</sub>)<sub>2</sub> revealed systematic absences ( $hkl$ ,  $h + k$  odd;  $h0l$ ,  $l$  odd) consistent with space groups  $Cc$  or  $C2/c$ . Subsequent refinement showed the latter to be correct. Data reduction yielded 2370 unique data with  $I > 3\sigma(I)$ . The position of the Ni atom was deduced from a

**Table II.** Atomic Coordinates ( $\times 10^4$ ) and Temperature Factors ( $\text{Å}^2 \times 10^3$ ) for [Ni(18S6)](pic)<sub>2</sub>

atom	x	y	z	U <sup>a</sup>
Ni	7500	7500	5000	25 (1)
S1	8626 (1)	7634 (1)	4915 (1)	32 (1)
S4	7529 (1)	4741 (1)	4994 (1)	33 (1)
S7	7386 (1)	7448 (2)	3707 (1)	34 (1)
C2	6229 (2)	5450 (6)	4717 (3)	36 (1)
C3	6690 (2)	4230 (5)	5003 (3)	36 (1)
C5	7739 (3)	4384 (6)	4068 (3)	43 (2)
C6	7435 (3)	5418 (6)	3481 (3)	44 (2)
C8	8137 (3)	8276 (6)	3477 (3)	43 (2)
C9	8720 (2)	7788 (6)	3949 (3)	45 (2)
O1	6289 (2)	9712 (5)	7286 (2)	66 (2)
O21	6352 (3)	7362 (6)	8310 (3)	97 (2)
O22	5381 (3)	6876 (7)	8514 (4)	113 (3)
O41	4390 (2)	1277 (6)	9623 (2)	70 (2)
O42	4661 (2)	3581 (6)	9311 (3)	82 (2)
O61	5948 (3)	4355 (6)	7360 (4)	111 (3)
O62	6526 (3)	2631 (6)	6952 (3)	87 (2)
N2	5802 (3)	7755 (6)	8370 (3)	68 (2)
N4	4700 (2)	2176 (6)	9264 (3)	52 (2)
N6	6119 (2)	3041 (6)	7342 (3)	47 (1)
C11	5975 (2)	297 (7)	7760 (3)	43 (2)
C12	5664 (3)	9406 (7)	8300 (3)	43 (2)
C13	5244 (3)	9977 (7)	8761 (3)	45 (2)
C14	5127 (2)	1548 (7)	8761 (3)	39 (2)
C15	5420 (2)	2520 (7)	8301 (3)	39 (1)
C16	5831 (2)	1922 (6)	7815 (3)	37 (1)

<sup>a</sup>Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table III.** Bond Lengths (Å) and Angles (deg) for [Ni(18S6)](pic)<sub>2</sub>

Ni–S1	2.389 (1)	Ni–S4	2.397 (1)
Ni–S7	2.377 (1)		
S1–C2	1.815 (5)	S1–C9'	1.806 (6)
S4–C3	1.823 (5)	S4–C5	1.814 (6)
S7–C6	1.816 (5)	S7–C8	1.812 (6)
C2–C3	1.510 (7)	C5–C6	1.515 (7)
C8–C9	1.519 (7)		
S4–Ni–S7	88.7 (1)	S4–Ni–S1	91.3 (1)
S7–Ni–S1	88.5 (1)		
Ni–S1–C9'	103.9 (2)	C2–S1–C9'	105.8 (2)
Ni–S4–C3	102.6 (2)	Ni–S4–C5	100.5 (2)
C3–S4–C5	105.1 (2)	Ni–S7–C6	104.1 (2)
Ni–S7–C8	101.1 (2)	C6–S7–C8	105.6 (3)
C3–C2–S1	115.0 (3)	S4–C3–C2	115.4 (3)
S4–C5–C6	116.8 (4)	S7–C6–C5	116.1 (4)
S7–C8–C9	116.3 (4)	C8–C9–S1'	116.5 (4)

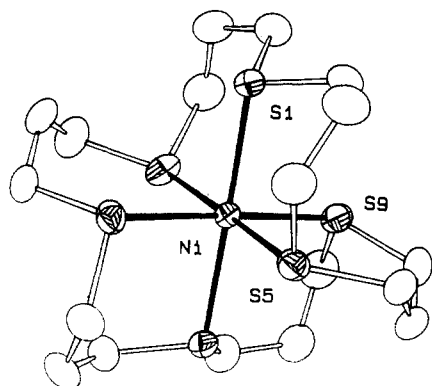
sharpened Patterson map; subsequent Fourier difference maps revealed the remaining non-hydrogen atoms. Full-matrix least-squares refinement converged to  $R = 4.81$  and  $R_w = 5.69$  for 189 parameters. The highest residual in the final difference map ( $1.0 \text{ e } \text{Å}^{-3}$ ) was associated with the anion centered on B2, which was disordered over the twofold axis. There were no indications of disorder in the [Ni(24S6)]<sup>2+</sup> cation.

[Ni(ttn)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> crystallizes with the cation disordered about a threefold axis. Partial refinement (with only some of the C atoms) gave  $R = 19.5$  with  $GOF = 3.924$  and unique Ni–S distances of 2.44 and 2.40 Å. While crystallographically unsatisfactory, these results establish the presence of an octahedral NiS<sub>6</sub> coordination sphere.

A complete listing of atomic coordinates, hydrogen atom coordinates, anisotropic temperature factors, and interatomic distances and angles for the first three structures is available as supplementary material.

## Results

**Description of the Structures.** Reaction of 18S6 with nickel(II) picrate affords [Ni(18S6)](pic)<sub>2</sub> (Figure 2), the first structurally characterized complex of this ligand.<sup>13</sup> It contains an octahedral centrosymmetric [Ni(18S6)]<sup>2+</sup> cation in which the high-spin Ni(II) ion coordinates to all six S atoms of 18S6, with Ni–S bond lengths of 2.389 (1), 2.397 (1), and 2.377 (1) Å (Table III). These bond lengths fall considerably short both of those observed previous in structures of octahedral nickel–thioether complexes (2.44 Å in [Ni(thiodiglycol)<sub>2</sub>(Br)<sub>2</sub>]<sup>22</sup> and [Ni(1,5-dithiacyclooc-



**Figure 3.** ORTEP drawing of the  $[\text{Ni}(24\text{S}6)]^{2+}$  cation showing thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity). Numbering of unique atoms follows the IUPAC convention, i.e., atoms are numbered sequentially around ring (S1, C2, etc.)

**Table IV.** Atomic Coordinates ( $\times 10^4$ ) and Temperature Factors ( $\text{\AA}^2 \times 10^4$ ) for  $[\text{Ni}(24\text{S}6)](\text{BF}_4)_2$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sup>a</sup></i>
Ni	0	-1599.7 (3)	7500	231
S1	1816.1 (6)	-1664.2 (5)	7675.3 (6)	301
S5	-405.7 (7)	-2677.6 (5)	6239.3 (6)	306
S9	-465.2 (7)	-584.0 (6)	6140.9 (7)	343
C2	1771 (3)	-1929 (3)	6381 (3)	404
C3	1623 (3)	-2796 (3)	6149 (4)	466
C4	798 (3)	-3217 (2)	6436 (3)	431
C6	-881 (3)	-2411 (3)	4853 (3)	398
C7	-1650 (3)	-1728 (3)	4590 (3)	415
C8	-1147 (4)	-925 (3)	4782 (3)	459
C10	-1450 (4)	90 (3)	6257 (4)	497
C11	-2466 (4)	-257 (3)	6227 (4)	464
C12	2380 (3)	-690 (3)	7786 (3)	442
B1	4389 (4)	-389 (3)	6435 (4)	470
B2	0	2048 (5)	7500	632
F11	5000	-760 (2)	7500	582
F12	3612 (4)	-879 (3)	5884 (3)	857
F13	3878 (5)	263 (3)	6586 (4)	1079
F14	5026 (4)	-174 (6)	6029 (4)	1150
F21	519 (7)	1562 (4)	7089 (6)	901
F22	590 (7)	2699 (5)	7472 (8)	1332
F23	742 (8)	1955 (6)	8619 (6)	1213

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

tane)<sub>2</sub>Cl<sub>2</sub>]<sup>23</sup>) and those predicted from the sum of ionic radii (also 2.44 Å).<sup>1</sup>

In the  $[\text{Ni}(18\text{S}6)]^{2+}$  cation the crown coordinates entirely in facial segments (i.e. each triad of adjacent S atoms occupies a trigonal face) to give the achiral meso isomer.<sup>10</sup> In this conformation each C-S-C-C fragment adopts gauche placement (supplementary material). Similar results have been reported for the analogous Co(II) complex.<sup>24,25</sup>

Coordination of the propyl-linked macrocycle 24S6 to Ni(II) yields  $[\text{Ni}(24\text{S}6)]^{2+}$  (Figure 3), the first structurally characterized complex of 24S6.<sup>14</sup> The  $[\text{Ni}(24\text{S}6)]^{2+}$  cation has twofold symmetry, and like its 18S6 analogue, it too contains an octahedral NiS<sub>6</sub> core. Unlike  $[\text{Ni}(18\text{S}6)]^{2+}$ , however, the Ni-S distances (2.413 (1), 2.437 (1), and 2.443 (1) Å) conform closely to the sum of ionic radii (Table V). Comparison with  $[\text{Ni}(18\text{S}6)]^{2+}$  shows that changing from the ethyl- to the propyl-linked macrocycle increases Ni-S bond lengths by 0.05 Å. In contrast to the 18S6 case, 24S6 coordinates to Ni(II) with two meridional (rather than facial) loops to give a racemic (rather than meso)

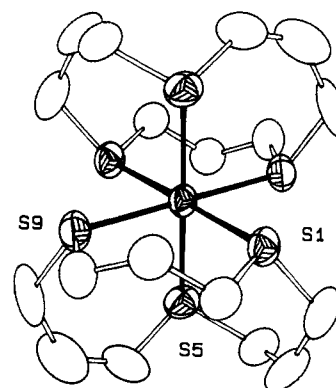
**Table V.** Bond Distances (Å) and Angles (deg) in  $[\text{Ni}(24\text{S}6)](\text{BF}_4)_2$

Ni-S1	2.413 (1)	Ni-S5	2.437 (1)
Ni-S9	2.443 (1)		
S1-C2	1.820 (4)	S1-C12	1.811 (4)
S5-C4	1.816 (4)	S5-C6	1.818 (4)
S9-C8	1.829 (4)	S9-C10	1.829 (5)
C2-C3	1.507 (7)	C3-C4	1.520 (6)
C6-C7	1.516 (7)	C7-C8	1.508 (6)
C10-C11	1.501 (7)	C11-C12'	1.511 (6)
S1-Ni-S1'	174.79 (5)	S5'-Ni-S1	87.60 (3)
S5-Ni-S1	88.48 (3)	S5-Ni-S5'	82.32 (4)
S9-Ni-S1'	90.48 (3)	S9-Ni-S1	93.21 (3)
S9-Ni-S5'	176.10 (4)	S9-Ni-S5	93.89 (3)
S9-Ni-S9'	89.92 (5)		
C2-S1-Ni	106.3 (1)	C12-S1-Ni	111.0 (2)
C12-S1-C2	99.0 (2)	C4-S5-Ni	109.6 (1)
C6-S5-Ni	116.7 (2)	C6-S5-C4	102.2 (2)
C8-S9-Ni	115.8 (2)	C10-S9-Ni	110.8 (2)
C10-S9-C8	101.0 (2)		
C3-C2-S1	113.6 (3)	C4-C3-C2	117.3 (3)
C3-C4-S5	116.9 (3)	C7-C6-S5	111.7 (3)
C8-C7-C6	115.2 (4)	C7-C8-S9	118.7 (3)
C11-C10-S9	117.5 (3)	C12'-C11-C10	115.2 (4)
C11'-C12-S1	113.7 (3)		

**Table VI.** Atomic Coordinates ( $\times 10^4$ ) and Temperature Factors ( $\text{\AA}^2 \times 10^4$ ) for  $[\text{Ni}(12\text{S}3)_2](\text{BF}_4)_2$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sup>a</sup></i>
Ni	0	0	0	370
S1	677.0 (8)	1615 (1)	76 (1)	469
S5	299.8 (9)	-561 (1)	1904 (1)	512
S9	900.0 (9)	-1075 (1)	-849 (1)	496
C2	759 (4)	2145 (5)	1496 (6)	642
C3	996 (5)	1385 (6)	2412 (6)	685
C4	463 (4)	575 (6)	2811 (5)	612
C6	1154 (6)	-1153 (11)	1888 (10)	1109
C7	1410 (6)	-1885 (9)	1235 (8)	1003
C8	1173 (6)	-2135 (6)	109 (8)	745
C10	1709 (4)	-432 (6)	-1182 (7)	624
C11	1659 (4)	767 (5)	-1384 (6)	577
C12	1574 (4)	1418 (5)	-310 (6)	579
B1	1665 (4)	5001 (7)	499 (8)	652
F1	1745 (3)	5493 (5)	-519 (4)	973
F2	2152 (3)	5483 (6)	1175 (5)	1188
F3	1046 (3)	5147 (6)	946 (5)	1195
F4	1837 (4)	3987 (4)	447 (7)	1300

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.



**Figure 4.** ORTEP drawing of the  $[\text{Ni}(12\text{S}3)_2]^{2+}$  cation showing thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity). Numbering of unique atoms follows the IUPAC convention; i.e., atoms are numbered sequentially around ring (S1, C2, etc.)

complex. In another contrast, six of the 12 C-S bonds adopt anti placement.

In  $[\text{Ni}(12\text{S}3)_2]^{2+}$  (Figure 4) two crown thioethers sandwich the metal ion, with each of them occupying a trigonal face. The

(22) Udupa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1981**, *52*, 215.

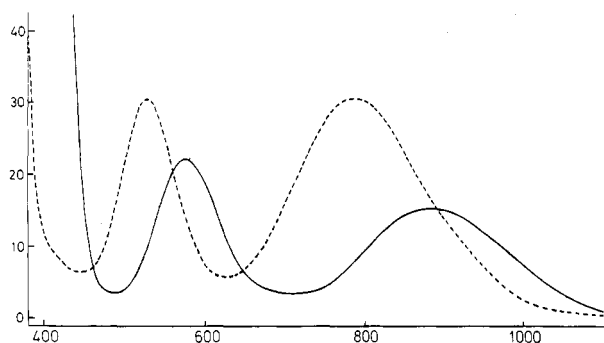
(23) Hill, N. L.; Hope, H. *Inorg. Chem.* **1974**, *13*, 2079.

(24) Hartman, J. R.; Hints, E. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1984**, 386.

(25) Hartman, J. R.; Hints, E. J.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1208.

**Table VII.** Bond Distances (Å) and Angles (deg) in [Ni(12S3)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>

Ni-S1	2.409 (1)	Ni-S5	2.435 (1)
Ni-S9	2.421 (2)		
S1-C2	1.817 (7)	S1-C12	1.813 (7)
S5-C4	1.809 (7)	S5-C6	1.81 (2)
S9-C8	1.823 (8)	S9-C10	1.805 (7)
C2-C3	1.52 (1)	C3-C4	1.52 (1)
C6-C7	1.30 (2)	C7-C8	1.45 (1)
C10-C11	1.52 (1)	C11-C12	1.52 (1)
S5-Ni-S1	94.40 (5)	S5-Ni-S1'	85.60 (5)
S9-Ni-S1	95.11 (5)	S9-Ni-S1'	84.89 (1)
S9-Ni-S5	93.10 (6)	S9-Ni-S5'	86.90 (6)
C2-S1-Ni	112.9 (2)	C12-S1-Ni	113.5 (2)
C12-S1-C2	101.5 (3)	C4-S5-Ni	111.6 (2)
C6-S5-Ni	109.0 (6)	C4-S5-C6	99.6 (7)
C8-S9-Ni	110.7 (3)	C10-S9-Ni	118.0 (2)
C10-S9-C8	102.2 (4)		
C3-C2-S1	117.6 (5)	C4-C3-C2	115.8 (7)
C3-C4-S5	117.1 (5)	S5-C6-C7	130 (1)
C6-C7-C8	125 (1)	C7-C8-S9	120.7 (7)
C11-C10-S9	114.8 (5)	C12-C11-C10	113.7 (6)
C11-C12-S1	112.9 (5)		

**Figure 5.** Optical spectra of the [Ni(9S3)<sub>2</sub>]<sup>2+</sup> (dashed line) and [Ni(12S3)<sub>2</sub>]<sup>2+</sup> (solid line) cations in CH<sub>3</sub>NO<sub>2</sub>.

resulting centrosymmetric cation has Ni-S distances of 2.409 (1), 2.421 (2), and 2.435 (1) Å, in close agreement with those of [Ni(24S6)]<sup>2+</sup> (Table VII). However, these distances exceed those in [Ni(9S3)<sub>2</sub>]<sup>2+</sup> by approximately 0.04 Å; thus, in both the tri- and hexadentate crown thioethers use of propyl-linked macrocycles substantially increases the average Ni-S distance.

Disorder vitiates detailed structural analysis of [Ni(ttn)<sub>2</sub>]<sup>2+</sup>. This cation crystallizes disordered over a threefold axis, which is incompatible with a bis(tridentate) complex. Nevertheless, although crystallographically unsatisfactory, X-ray diffraction does establish the existence of the Ni<sub>6</sub> coordination sphere, as also indicated by the optical studies described below. A Job's plot for the Ni(II)-2,5,8-trithianonane system (supplementary material) confirmed formation of the bis complex in nitromethane solution.

**Electronic Spectroscopy.** Of the three d-d bands expected for octahedral Ni(II) ions (<sup>3</sup>A<sub>2</sub> → <sup>3</sup>T<sub>2</sub>, <sup>3</sup>A<sub>2</sub> → <sup>3</sup>T<sub>1</sub>(F), <sup>3</sup>A<sub>2</sub> → <sup>3</sup>T<sub>1</sub>(P)), only the first two are observable in the [Ni(thioether)<sub>6</sub>]<sup>2+</sup> complexes examined here (Figure 5; Table VIII). The highest energy (<sup>3</sup>A<sub>2</sub> → <sup>3</sup>T<sub>1</sub>(P)) band is obscured by a charge-transfer band starting around 400 nm. Comparison with results from selected amine complexes (Table VIII) shows (1) that thioethers and amines exert roughly comparable ligand field strengths<sup>26</sup> but (2) that thioethers manifest a much greater nephelauxetic effect. Nephelauxetic ratios ( $\beta = B_{\text{complex}}/B_{\text{free ion}}$ ) for the thioether complexes average approximately 0.7, while those for the amine complexes all equal or exceed 0.9. The low nephelauxetic ratio for the thioether complexes implies considerable mixing between ligand and metal orbitals. This mixing in turn accounts for the strong stabilization of lower oxidation<sup>27,28</sup> and spin<sup>24,25</sup> states

**Table VIII.** Electronic Spectra,<sup>a</sup> Ligand Field Parameters, and Magnetic Moments of Nickel(II) Crown Thioether Complexes and Comparison with Selected Amine Complexes

complex <sup>c</sup>	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	$\Delta$ , cm <sup>-1</sup>	$\beta^b$	$\mu_{298}$ , $\mu_B$	ref
[Ni(18S6)] <sup>2+</sup>	815 (23) 520 (27)	12 290	0.83	2.77	d
[Ni(9S3) <sub>2</sub> ] <sup>2+</sup>	790 (30) 530 (30)	12 650	0.66	3.05, 2.83	12, d, e
[Ni(12S3) <sub>2</sub> ] <sup>2+</sup>	890 (25) 570 (34)	11 240	0.74	3.19, 3.07	9, d
[Ni(24S6)] <sup>2+</sup>	905 (100) 590 (70)	11 050	0.66	f	d
[Ni(ttn) <sub>2</sub> ] <sup>2+</sup>	847 (21) 553 (14)	11 800	0.70	2.80	d
[Ni(dth) <sub>3</sub> ] <sup>2+</sup>	900 (37) 575 (33)	10 900	0.75	3.15	31, 9
[Ni(L)] <sup>2+</sup>	816 (107) 549 (97)	12 250	0.63	2.93	g
[Ni(18N6)] <sup>2+</sup>	893 (21) 552 (64)	11 200	0.93	2.57	h
[Ni(9N3) <sub>2</sub> ] <sup>2+</sup>	800 (7) 505 (5)	12 500	0.90	2.8	i
[Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	930 570	10 750	0.95	f	j

<sup>a</sup>Includes only <sup>3</sup>A<sub>2</sub> → <sup>3</sup>T<sub>2</sub> and <sup>3</sup>A<sub>2</sub> → <sup>3</sup>T<sub>1</sub>(F) transitions; <sup>3</sup>A<sub>2</sub> → <sup>3</sup>T<sub>1</sub>(P) falls under the edge of the charge-transfer band. <sup>b</sup>Calculated from  $B = 2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2 / (15\nu_2 - 27\nu_1)$ ; in the free ion  $B = 1038$  cm<sup>-1</sup>. <sup>c</sup>Key: dth = 2,5-dithiahexane; ttn = 2,5,8-trithianonane; L = 1,1,1-tris((2-(methylthio)ethyl)thio)ethane; 9N3 = 1,4,7-triazacyclononane; 18N6 = 1,4,7,10,13,16-hexaazacyclooctadecane. <sup>d</sup>This work. <sup>e</sup>Wiegardt, K.; Küppers, H.-J.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 3067. <sup>f</sup>High spin. <sup>g</sup>Thorne, C. M.; Rawle, S. C.; Admans, G. A.; Cooper, S. R. *Inorg. Chem.* **1986**, *25*, 3848. <sup>h</sup>Hay, R. W.; Jeragh, B.; Lincoln, S. F.; Searle, G. H. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 435. <sup>i</sup>Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1980**, *45*, L263 and references therein. <sup>j</sup>Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, PA, 1977; p 382.

observed in earlier work on other transition metals.

## Discussion

Each of the crown thioether complexes examined here — [Ni(18S6)]<sup>2+</sup>, [Ni(12S3)<sub>2</sub>]<sup>2+</sup>, and [Ni(24S6)]<sup>2+</sup>—comprises a six-coordinate NiS<sub>6</sub> coordination sphere in which the crown thioether(s) wrap around the high-spin Ni(II) ion. Thus the present ligands provide a way to impose three- and sixfold thioether coordination on a metal ion; they therefore complement 14S4, which can enforce fourfold thioether coordination as in the low-spin square-planar complex [Ni(14S4)]<sup>2+</sup>.<sup>29,30</sup>

Compared to simple dialkyl thioethers (e.g. Me<sub>2</sub>S), the crown thioethers 9S3, 12S3, 18S6, and 24S6 all yield particularly robust octahedral [Ni(thioether)]<sup>2+</sup> complexes. (For example, [Ni(SMe<sub>2</sub>)<sub>6</sub>]<sup>2+</sup> cannot be made at all, while even [Ni(dth)<sub>3</sub>]<sup>2+</sup> (dth = 2,5-dithiahexane)<sup>31</sup> forms only in the presence of a large excess of ligand.) Thioethers generally bind weakly because they are both weak  $\sigma$ -donors and weak  $\pi$ -acceptors.<sup>1</sup> In addition, coordination of several simple dialkyl thioethers to one metal ion engenders serious steric repulsions between the alkyl substituents from different ligands. Incorporation of thioethers into a crown-type structure, however, can greatly enhance their tendency to coordinate. Three factors can contribute to this greater stability:

- (27) Rorabacher, D. B.; Martin, M. J.; Koenigbauer, M. J.; Malik, M.; Schroeder, R. R.; Endicott, J. F.; Ochrymowycz, L. A. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Gunderland, NY, 1983; pp 167-202. Diaddario, L. L., Jr.; Dockal, E. R.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1985**, *24*, 356 and references therein.
- (28) Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1202.
- (29) Davis, P. H.; White, L. K.; Belford, R. L. *Inorg. Chem.* **1975**, *14*, 1753.
- (30) Interestingly, treatment of [Ni(14S4)]<sup>2+</sup> with neat Me<sub>2</sub>S affords a material with an optical spectrum consistent with that expected for [Ni(14S4)(Me<sub>2</sub>S)]<sup>2+</sup>.
- (31) Flint, C. D.; Goodgame, M. J. *Chem. Soc. A* **1968**, 2178.

(26) Carlin, R. L.; Weissberger, E. *Inorg. Chem.* **1964**, *3*, 611.

**Table IX.** Summary of Structural Features of Nickel(II) Crown Thioether Complexes

	ligand			
	18S6	(9S3) <sub>2</sub> <sup>a</sup>	(12S3) <sub>2</sub>	24S6
∠S-Ni-S(chel), deg	89.5	88.5	94.2	91.0
∠S-Ni-S'(nonchel), deg	90.5	91.5	85.8	88.3
trig twist angle, deg	60	60	60	59.3
Ni-S dist, Å	2.39	2.39	2.42	2.43
chel S...S, Å	3.36	3.33	3.55	3.47
nonchel S...S, Å	3.39	3.42	3.30	3.39
ligand bite, Å	1.41	1.39	1.47	1.43

<sup>a</sup> From ref 12.

(1) the chelate effect, (2) the macrocyclic effect (but see ref 32), and (3) the elimination of steric repulsions between alkyl substituents.

Among crown thioether complexes those of 9S3 exhibit particular stability. This has previously been attributed to the unusual conformation of the free ligand, which needs to change very little to coordinate to a metal ion.<sup>12,33</sup> Indeed, ligand conformational factors in general profoundly influence the stability of crown thioether complexes. Previous work<sup>34,35</sup> has revealed the substantial conformational change required for coordination of 12S3. The enthalpic price of enforcing this change must decrement the stability of the resulting complex. Consistent with this view, [Ni(12S3)<sub>2</sub>]<sup>2+</sup> decomposes immediately on contact with water<sup>8</sup> or even with a humid atmosphere. (Similar behavior is found for [Ni(24S6)]<sup>2+</sup>.) In contrast, [Ni(9S3)<sub>2</sub>]<sup>2+</sup> resists ligand displacement so strongly that it can be recrystallized from water.

This difference between the complexes of ethyl-linked (9S3 and 18S6) and propyl-linked (12S3 and 24S6) ligands focuses attention on the consequences of the extra methylene unit in the latter. Examination of the thermal ellipsoids in the [Ni(12S3)<sub>2</sub>]<sup>2+</sup> structure reveals serious disorder of C6 and C7; in addition, the three six-membered Ni-S-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S chelate rings adopt chair, flattened-chair, and twist-boat conformations. This conformational heterogeneity parallels that observed previously for [Ru(12S3)<sub>2</sub>]<sup>2+</sup> and reflects the unsuitability of 12S3 for coordination to a trigonal face.

(32) Margerum, D. W.; Smith, G. F. *J. Chem. Soc., Chem. Commun.* **1975**, 807.

(33) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068.

(34) Rawle, S. C.; Admans, G. A.; Cooper, S. R. *J. Chem. Soc., Dalton Trans.* **1988**, 93.

(35) Rawle, S. C.; Sewell, T. J.; Cooper, S. R. *Inorg. Chem.* **1987**, *26*, 3769.

The conformational constraints of the ligands also manifest themselves in deformations of the NiS<sub>6</sub> core (Table IX). Their impact appears in both the molecular and electronic structures of the complexes. The two ethyl-linked macrocycles yield average Ni-S distances 0.06 Å shorter than the sum of ionic radii (2.38 vs 2.44 Å). In contrast, average Ni-S distances in [Ni(12S3)<sub>2</sub>]<sup>2+</sup> and [Ni(24S6)]<sup>2+</sup> (2.42 and 2.43 Å) closely approach the expected value.

This macrocyclic constriction effect<sup>36</sup> also manifests itself in ligand field parameters, which divide the complexes into two classes. The ligand field splittings in [Ni(18S6)]<sup>2+</sup> and [Ni(9S3)<sub>2</sub>]<sup>2+</sup> exceed those in [Ni(12S3)<sub>2</sub>]<sup>2+</sup> and [Ni(24S6)]<sup>2+</sup> (and [Ni(ttn)<sub>2</sub>]<sup>2+</sup>) by 10%. Hence replacement of a propyl-linked macrocycle with an ethyl-linked one increases Δ in the course of constricting the Ni-S coordination sphere. These results supplement earlier work on ring size effects by Busch<sup>37</sup> and Rorbacher<sup>27</sup> and their co-workers.

### Conclusion

The present results show that thioethers exert ligand field splittings roughly comparable with those of amines, but with a considerably greater nephelauxetic effect. This cloud-expanding ability apparently accounts for the salient characteristics of thioether coordination observed in previous work: the strong stabilization of lower spin and oxidation states. This work also demonstrates the considerable magnitude by which the electronic properties of a metal ion can be tuned within the context of a conserved coordination sphere.

**Acknowledgment.** This work has been supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, by the Office of Health and Environmental Research, U.S. Department of Energy, Contract No. DE-AC03-76SF00472, and by the Science and Engineering Research Council (U.K.).

**Registry No.** [Ni(ttn)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 113056-24-9; [Ni(18S6)](pic)<sub>2</sub>, 33270-88-1; [Ni(18S6)](CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, 113056-25-0; [Ni(12S3)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 25640-50-0; [Ni(24S6)](BF<sub>4</sub>)<sub>2</sub>, 106007-09-4.

**Supplementary Material Available:** Tables containing bond distances and angles, anisotropic thermal parameters, hydrogen atomic coordinates, and torsional angles and a Job's plot for [Ni(ttn)<sub>2</sub>]<sup>2+</sup> (11 pages); structure factor tables (37 pages). Ordering information is given on any current masthead page.

(36) Hung, Y.; Martin, L. Y.; Jackels, S. C.; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 4029.

(37) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2967 and references therein.