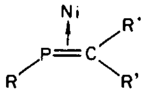
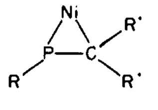
being Ni (−0.08), P(1) (−0.17), P(2) (0.12), P(3) (−0.07), and C(8) (0.21). The P–C bond length of 1.773 (8) Å in **4** is approximately midway between the P–C single-bond length of 1.85 Å and the P═C bond length of 1.67 Å which has been reported for uncoordinated phosphaalkenes.[13,14] Alkenes and diphosphenes undergo comparable increases of C═C or P═P bond length upon η^2 ligation.[5,6] The sum of bond angles at C(8) in **4** is 343.5°, indicating that the hybridization of the phosphaalkene carbon is approximately halfway between sp^2 and sp^3. The Si(3)–C(8)–Si(4) and C(1)–P(1)–C(8) bond angles in **4** are very similar to those exhibited by uncoordinated phosphaalkenes.[13,14] In valence bond terminology the bonding in **4** can be described as a resonance hybrid of π-bonded (I) or metallacyclic (II)[15] canonical forms.



I



II

From a molecular orbital standpoint the bonding in **4** is probably best represented as a dative π interaction. For example, MO calculations[16] on the model complex $Ni(PH_3)_2(C_2H_4)$ have revealed that the major contributor to ethene bonding is back-donation from a filled Ni 3d AO to the vacant olefinic π^* MO. Since MO calculations on HP═CH$_2$[17] and HP═PH[18] indicate the existence of low-lying π^* MO's, it is reasonable to suggest retro π-bonding as the primary bonding interaction in η^2 phosphaalkene (**2**) and diphosphene (**3**) complexes.

The square-planar geometry for **4** evidently persists in solution since the 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum comprises an ABX pattern. Computer simulation by routine methods afforded the parameters $\delta_{P(A)}$ −18.2, $\delta_{P(B)}$ −19.7, $\delta_{P(X)}$ +23.4, $J_{P(A)P(X)} = 45.8$, $J_{P(B)P(X)} = 28.6$, $J_{P(A)P(B)} = 27.0$ Hz. We have recently prepared the uncoordinated phosphaakene (Me$_3$Si)$_2$C═PC(H)(SiMe$_3$)$_2$ (**5**), for which $\delta_P = +404$.[9] In contrast to the η^1 (P bonded) phosphaalkene complexes,[1,2] a pronounced (>380 ppm) upfield coordination chemical shift thus accompanies η^2 complexations of **5**. This observation is consistent with back-donation from Ni 3d AO's to the phosphaalkene π^* MO.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for generous financial support.

Note Added in Proof. Evidence has been presented recently for η^2-bonding of a phosphaalkene to Pt in solution. However, in the crystalline state the phosphaalkene was η^1-bonded.[19]

Registry No. 4, 85650-29-9.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, thermal parameters, and structure factors (13 pages). Ordering information is given on any current masthead page.

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(16) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292.

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Crown Thioether Chemistry. The Nickel(II) Complex of 1,4,7,10,13,16-Hexathiacyclooctadecane, the Hexathia Analogue of 18-Crown-6

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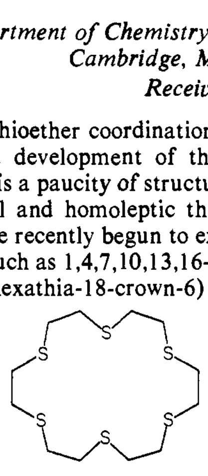
The discovery of thioether coordination to Cu(II) in plastocyanin[1] has spurred development of thioether coordination chemistry, but there is a paucity of structural data on thioether complexes in general and homoleptic thioether complexes in particular.[2] We have recently begun to examine the chemistry of crown thioethers such as 1,4,7,10,13,16-hexathiacyclooctadecane[3] (I) (hereafter hexathia-18-crown-6) as a first step toward using them as ligands and were particularly intrigued by the early report of Black and McLean[4,5] that hexathia-18-crown-6 forms 1:1 complexes with Ni(II) picrate (as indicated by elemental analysis). We have examined this latter compound by diffraction methods and found it to be a unique octahedral complex with the *crown thioether wrapped around the metal ion.* This compound represents to our knowledge the first structurally characterized example of an octahedral transition-metal complex bound solely by thioether ligands.[6]



I

Hexathia-18-crown-6 (10 mg, 0.03 mmol; prepared as described previously[3,7]) was dissolved in 5 mL of acetone; upon addition of a refluxing solution of nickel picrate (15 mg, 0.03 mmol) in 5 mL of acetone the light yellow-green solution became bright yellow. After refluxing for 20 min, the solution was allowed to cool. The orange crystalline product was collected by filtration and dried in vacuo overnight, yield 0.019 g (80%). Anal. Calcd (Galbraith Laboratories, Knoxville, TN) for $C_{24}H_{28}N_6O_{14}S_6Ni$: 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 CH_3CN afforded beautiful orange monoclinic prisms suitable for X-ray diffraction studies. Crystal data: space group $C2/c$, $a = 21.079$ (6) Å, $b = 8.685$ (2) Å, $c = 18.399$ (5) Å, $\beta = 93.63$ (2)°; d_{calcd}, 1.73 g/cm^3, $Z = 4$; 2889 unique reflections with $F > 3\sigma(F)$ were collected with a Syntex R3 diffractometer with use of Mo Kα (0.71069 Å) radiation. The structure was solved by heavy atom methods and refined by cascade block-diagonal least-squares methods (with anisotropic thermal parameters for all non-hydrogen atoms). At the present stage of refinement $R = 6.2\%$ and $R_w = 5.8\%$.[8,9]

In [Ni(II)·hexathia-18-crown-6]$^{2+}$ the nickel(II) ion is on a center of symmetry and is neatly encapsulated within the hexathia-18-crown-6 ligand (Figure 1). Hexathia-18-crown-6 wraps

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(1) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature (London)* **1978**, *272*, 319–24.

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(5) Black, D. St. C.; McLean, I. A. *Aust. J. Chem.* **1971**, *24*, 1401–11.

(6) Several examples of octahedral Ni(II) coordinated only by thioethers have been reported, although not characterized structurally. See: Rosen, W.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 4694–7. Rosen, W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 262–5. Flint, C. D.; Goodgame, M. *J. Chem. Soc. A* **1968**, 2178–82.

(7) Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079–84.

(8) $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and $w = 1/\sigma^2F + 0.001F^2$.

(9) Tables of positional and thermal parameters are available as supplementary material.

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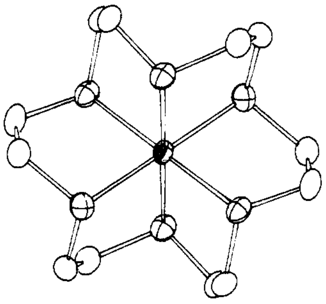

Figure 1. ORTEP drawing of the Ni^{II}(picrate)$_2$ complex of 1,4,7,10,13,16-hexathiacyclooctadecane (hexathia-18-crown-6) showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity).

around the metal ion to yield the achiral meso geometric isomer in which each $-S(CH_2)_2S(CH_2)_2S-$ segment of the ligand coordinates to a trigonal face of the metal ion (facial coordination).[10,11] The NiS_6 coordination sphere is essentially octahedral: the *cis*-S–Ni–S bond angles are 90 ± 1.5° (range 88.5–91.3°), while the *trans*-S–Ni–S bond angles are required by the inversion symmetry to be 180°. The [Ni(II)·hexathia-18-crown-6]$^{2+}$ cation closely approaches D_{3d} ($\bar{3}m$) symmetry, which is the maximum symmetry possible for this complex. Approximately pseudo-tetrahedral geometry is found at all of the sulfur atoms, with bond angles decreased somewhat from the tetrahedral value. This decrease is typical of metal–thioether complexes and has been attributed to the steric effect of the remaining sulfur lone-pair electrons.[2]

The Ni–S bond lengths in [Ni(II)·hexathia-18-crown-6]$^{2+}$ at 2.376 (1), 2.389 (1), and 2.397 (1) Å are all considerably shorter than the 2.44 Å predicted from the covalent radii of Ni(II) (1.39 Å) and thioether sulfur (1.05 Å).[2,12] Furthermore, the Ni(II)–S bond lengths found here are also short in comparison with those found in earlier structures. For example, a Ni–S distance of 2.431 (1) Å was found in $Ni(thiodiglycol)_2(Br)_2$[13] while Ni(1,5-dithiacyclooctane)$_2$Cl$_2$[14] has Ni–S distances of 2.478 (3) and 2.497 (3) Å, compared with the average value of 2.39 Å observed here. From molecular models it appears that any increase in the Ni–S bond lengths of [Ni(II)·hexathia-18-crown-6]$^{2+}$ from the observed values would cause considerable strain in the macrocycle. We suggest that the short Ni–S bond lengths of hexathia-18-crown-6 derive from the "macrocyclic constriction" effect:[15,16] hexathia-18-crown-6 compresses the Ni–S bonds in order to minimize strain in the ligand. Hence the metal–ligand fit is not perfect, despite the lack of angular distortion in the NiS_6 unit. Since the ligand itself has bond distances comparable to those of free hexathia-18-crown-6,[3,17] apparently the intraligand and not the Ni–S interactions dominate in determining the Ni–S bond lengths.

While the macrocycle strongly influences the Ni–S bond lengths, the nickel ion determines the *geometry* of the complex. In crown ether–alkali metal ion complexes electrostatic considerations and the fit of the metal ion in the cavity determine the geometry of the complex. In contrast, in [Ni(II)·hexathia-18-crown-6]$^{2+}$ the rigid sterochemical demands of the transition-metal ion dictate the geometry of the complex. Comparison of the Ni(II) complex of hexathia-18-crown-6 with the K$^+$ complex of 18-crown-6 underscores this point. Although both [K·18-crown-6]$^+$ and [Ni(II)·hexathia-18-crown-6]$^{2+}$ have idealized D_{3d} symmetry, the two complexes differ markedly in the extent of compression along the trigonal pseudoaxis. In the former the six oxygen atoms are nearly coplanar, with only 0.38 Å between the top and bottom trigonal faces.[18] In contrast, in [Ni(II)·hexathia-18-crown-6]$^{2+}$ the transition-metal ion enforces octahedral geometry on the sulfur atoms and thereby causes those on opposite trigonal faces to be 2.78 Å apart. In a planar arrangement hexathia-18-crown-6 would have about the same "cavity size" as 18-crown-6, since the larger size of the sulfur atoms is roughly offset by the longer C–S bond length.[19] However, the octahedral stereochemistry about Ni(II) decreases the effective cavity diameter of hexathia-18-crown-6 by approximately a factor of 2.

Several conclusions can be drawn from the present work. This structure proves that hexathia-18-crown-6 can wrap around a transition-metal ion to afford octahedral coordination. Moreover, since hexathia-18-crown-6 forces the Ni(II) ion to accept unusually short Ni–S distances, ionic radius–cavity size arguments clearly cannot be applied rigidly to predict which transition-metal ions will form complexes with hexathia-18-crown-6. In addition, the unusual Ni–S bond lengths found here strongly suggest that unusual reaction chemistry may be found as well. Further studies of the coordination chemistry of this and related ligands are presently underway.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corp. for support of this research. The purchase of the diffractometer was supported in part by NSF grant CHE 8000670.

Registry No. [Ni^{II}·hexathia-18-crown-6](picrate)$_2$, 33270-88-1.

Supplementary Material Available: Listings of atomic positional and thermal parameters and of interatomic distances and angles (5 pages). Ordering information is given on any current masthead page.

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(10) Very recently Royer et al. reported the structure (Royer, D. J.; Grant, G. J.; Van Derveer, D. G.; Castillo, M. J. *Inorg. Chem.* **1982**, *21*, 1902–8) of the racemic isomer of [Co(III)·1,4,7,10,13,16-hexaazacyclooctadecane]$^{2+}$ (the hexaamine analogue of hexathia-18-crown-6), in which two $-N(CH_2)_2N(CH_2)_2N-$ segments coordinate in a meridional fashion.

(11) For other reports on the hexaamine analogue of hexathia-18-crown-6 see: Yoshikawa, Y. *Chem. Lett.* **1978**, 109–112. Searle, G. H.; Dwyer, M.; *Inorg. Chim. Acta* **1981**, *52*, 251–5. Hay, R. W.; Jeragh, B.; Lincoln, S. F.; Searle, G. H. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 435–40.

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(14) Hill, N. L.; Hope, H.; *Inorg. Chem.* **1974**, *13*, 2079–82.

(15) Hung, Y.; Martin, L. Y.; Jackels, S. C.; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 4029–39.

(16) Martin, L. Y.; DeHayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4046–8.

(17) The individual bond lengths of hexathia-18-crown-6 in an asymmetric unit are (Å) S(1)–C(9a) 1.809 (5), S(1)–C(2) 1.814 (5), S(4)–C(3) 1.823 (5), S(4)–C(5) 1.813 (6), S(7)–C(6) 1.814 (5), S(7)–C(8) 1.812 (5), C(2)–C(3) 1.512 (6), C(5)–C(6) 1.516 (7), C(8)–C(9) 1.518 (7).

(18) Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2744–5.

(19) This point has been emphasized recently. See ref 12.

Sesbanimide, a Potent Antitumor Substance from *Sesbania drummondii* Seed

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We have reported previously that extracts from seeds of *Sesbania drummondii* (Rydb.) Cory (Fabaceae) have pronounced antitumor activity in experimental systems.[1-3] We now report

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[†] The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.