$(Me_3P)_2PtEt_2$, 76136-98-6; $(Et_3P)_2PtPr_2$, 76189-29-2; $(Et_3P)_2Pt(C_4H_7)_2$, 76156-55-3; $(Et_3P)_2Pt(C_5H_9)_2$, 76136-99-7; $(Ph_3P)_2Pt(C_4H_7)_2$, 76137-00-3; $(DMPE)PtEt_2$, 76137-01-4; $(COD)PtCl_2$, 12080-32-9; *trans*-$(Et_3P)_2Pt(Me)I$, 18974-13-5; MeI, 74-88-4; cyclobutylmagnesium chloride, 76124-42-0; cyclopentylmagnesium bromide, 33240-34-5.

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Nickel(II) Complexes of New S_2N_2-Donor Macrocycles. Synthesis and Kinetics of Dissociation

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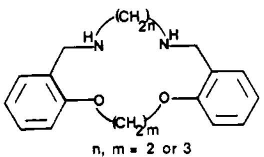
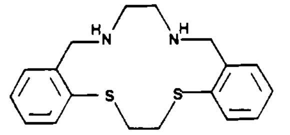
Transition-metal complexes of macrocyclic ligands incorporating N_4- and S_4-donor sets have been well investigated (especially for studies concerning the nature of the macrocyclic effect).[1] With nickel(II), the N_4 systems are usually very kinetically inert[2] (and thermodynamically stable) whereas the S_4 macrocycles yield complexes which are much more labile.[3] The metal-ion chemistry of S_2N_2 macrocycles has received less attention, and few such ligands have been reported previously.[4-6]

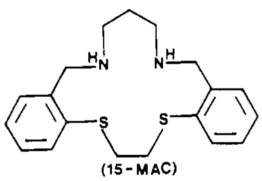
As an extension of our recent studies involving O_2N_2-donor macrocycles of type **1**,[7-9] the syntheses of the analogous S_2N_2-donor macrocycles **2**-**4** are now reported. Since thioether donors tend to have stronger affinities for nickel(II) than do ether donors, the nickel complexes of the new macrocycles might mainly be expected to exhibit labilities which fall between those of O_2N_2-donor and N_4-donor macrocyclic complexes. We present here a report of the interaction of nickel with the new 14- to 16-membered macrocycles of types **2**-**4** together with a study of the kinetics of dissociation of the nickel complex of the 15-membered ring.



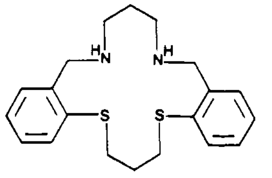
n, m = 2 or 3
1



(14-MAC)
2



(15-MAC)
3



(16-MAC)
4

Experimental Section

The instrumentation used for the physical measurements has been described previously.[7-9] Infrared spectra were obtained on Nujol mulls of the compounds, the spectrophotometer was calibrated against a polystyrene standard. ^1H and ^{13}C NMR chemical shifts are relative to tetramethylsilane (Me_4Si) for $CDCl_3$ solutions and 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for D_2O solutions.

The kinetic study was performed in aqueous media ($I = 1.0$) under conditions identical with those described previously.[8] The dissociation was followed spectrophotometrically at 600 nm. The consecutive rate constants were obtained with the aid of a computer program described elsewhere.[10]

1,4-Bis(2-benzyl alcohol)-1,4-dithiabutane. A stirred suspension of 1,4-bis(2-carboxyphenyl)-1,4-dithiobutane (33.4 g), prepared as described previously,[11] in ether (300 mL) was slowly added to a stirred suspension of $LiAlH_4$ (8.0 g) in ether (600 mL). The mixture was refluxed under N_2 for 100 h and then cooled to 0 °C. Excess $LiAlH_4$ was destroyed by careful dropwise addition of water (8 mL), 15% NaOH (8 mL), and then water (24 mL).[12] The gelatinous white solid was filtered off and dried by mixing with an equal weight of Na_2SO_4. This mixture was then extracted several times with hot chloroform. The extracts were combined with the ether filtrate, and this was then evaporated to dryness to yield crude product which was recrystallized from chloroform to yield white needles: yield 40%; mp 111 °C; mass spectrum parent ion *m/e* 306. Anal. Calcd for $C_{16}H_{18}O_2S_2$: C, 62.7; H, 5.9. Found: C, 62.4; H, 6.1. The IR spectrum contained a broad OH stretching band in the region 3220-3320 cm^{-1}.

1,5-Bis(2-benzyl alcohol)-1,5-dithiapentane. A similar procedure to the above yielded this diol as an oil (yield 45%) which was characterized by NMR and used without further purification. ^1H NMR ($CDCl_3$): 1.89 (quintet, SCH_2CH_2), 3.01 (t, SCH_2), 4.78 (s, CH_2OH), 7.20-7.55 (m, aromatic). The IR spectrum was very similar to that of the above compound and contained a broad OH stretching band in the region 3220-3320 cm^{-1}.

1,4-Bis(2-formylphenyl)-1,4-dithiabutane. A mixture of 1,4-bis(2-benzyl alcohol)-1,4-dithiabutane (6.2 g) in ether and excess activated manganese dioxide (MnO_2—type B)[13] was refluxed for 24 h. MnO_2 was filtered off and washed several times with hot chloroform, and the wash solutions were combined with the ether filtrate. The solution was evaporated to dryness to yield the product. Recrystallization from ether gave white crystals: yield 95%; mp 136 °C (lit. 137 °C).[14] IR: $\nu_{C=O}$ 1675 cm^{-1}. ^1H NMR ($CDCl_3$): 3.10 (s, CH_2), 7.10-7.75 (m, aromatic), 10.16 (s, CHO).

1,5-Bis(2-formylphenyl)-1,5-dithiapentane. A procedure similar to the above converted the corresponding diol to the required product as white crystals after recrystallization from methanol: yield 90%; mp 56-57 °C. IR: $\nu_{C=O}$ 1675 cm^{-1}. ^1H NMR ($CDCl_3$): 2.05 (quintet, SCH_2CH_2), 3.01 (t, SCH_2), 7.12-7.83 (m, aromatic), 10.38 (s, CHO).

General Preparation for the S_2N_2-Donor Macrocycles. Diamine (1,2-diaminoethane or 1,3-diaminopropane; 0.01 mol) in dry methanol (50 mL) was slowly added to a stirred solution of the appropriate dialdehyde (0.01 mol) in dry methanol (300 mL). Borax[15] (0.5 g) and then $NaBH_4$ (1.0 g) were added, and the solution was concentrated to 80 mL. Water (300 mL) was added, and the solution was extracted with chloroform (three times). The extracts were dried over anhydrous sodium sulfate and were then added to an equal volume of dry ether. Dry HCl gas was passed through this solution, and the white solid

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Table I. Physical Data for the Nickel(II) Complexes

complex	color	infrared^{a,b} ν_{NH}, cm^{-1}	μ_{eff}^{c}	visible reflectance spectra,^{a,d} nm
$Ni_2(14\text{-}MAC)Cl_4 \cdot {}^1/_2BuOH$	purple	3225, 3125	3.11	500, 555 (sh), 1020
$Ni(15\text{-}MAC)Cl_2 \cdot {}^1/_2H_2O$	blue	3255, 3225	3.21	630, 860, ~1160 (w, sh)^{e}
$Ni(16\text{-}MAC)Cl_2 \cdot H_2O$	green	3200	3.25	660, 1190

[a] Nujol mull spectra. [b] All complexes also showed a broad ν_{OH} in this region. [c] Value per nickel ion. [d] Spectral range scanned 365-1350 nm; no peak is listed for the 370-420-nm region as the edge of an intense absorption (ligand, d-d, and/or charge transfer) occurs in this region. [e] This complex in dichloromethane gave the following spectrum (in nm): 360 (sh), 625 (ϵ = 23.8 M^{-1} cm^{-1}), 875 (ϵ = 17.0 M^{-1} cm^{-1}), 1120 sh. The other two complexes in the series were not sufficiently soluble to obtain solution spectra.

which separated was recrystallized from a hydrochloric methanol/acetone solution to yield the product as the hygroscopic dihydrochloride; yield ~40% in each case. Anal. Calcd for 14-MAC·2HCl·H_2O, $C_{18}H_{26}Cl_2N_2S_2O$: C, 51.3; H, 6.2; N, 6.6. Found: C, 50.9; H, 6.0; N, 6.4. Mass spectrum parent iron *m/e* 330. ^{1}H NMR (D_2O): 3.50 (s, NCH_2), 3.61 (s, aromatic CH_2), 4.40 (s, SCH_2), 7.23–7.68 (m, aromatic). ^{13}C NMR (D_2O): 35.8 (t, NCH_2), 44.4 (t, aromatic CH_2), 51.0 (t, SCH_2), 130.6–134.9 (aromatic). Anal. Calcd for 15-MAC·2HCl·1.5H_2O, $C_{19}H_{29}Cl_2N_2S_2O_{1.5}$: C, 51.4; H, 6.6; N, 6.3. Found: C, 51.4; H, 6.4; N, 6.1. Mass spectrum parent ion *m/e* 344. ^{1}H NMR ($CDCl_3$): 1.77 (quintet, NCH_2CH_2), 1.83 (s, NH), 2.74 (t, NCH_2), 3.17 (s, aromatic CH_2), 3.79 (s, SCH_2), 7.12–7.43 (m, aromatic). ^{13}C NMR ($CDCl_3$): 29.9 (t, NCH_2CH_2), 33.4 (t, NCH_2), 48.5 (t, aromatic CH_2), 53.4 (t, SCH_2), 126.9–141.0 (aromatic). Anal. Calcd for 16-MAC·2HCl·H_2O, $C_{20}H_{30}Cl_2N_2S_2O$: C, 53.5; H, 6.5; N, 6.2. Found: C, 53.6; H, 6.7; N, 6.1. Mass spectrum parent ion *m/e* 358. ^{1}H NMR ($CDCl_3$): 1.69 (quintet, NCH_2CH_2), 1.75 (s, NH), 1.92 (quintet, SCH_2CH_2), 2.66 (t, NCH_2), 3.02 (t, SCH_2), 3.85 (s, aromatic CH_2), 7.12–7.44 (m, aromatic). ^{13}C NMR ($CDCl_3$): 28.9 (t, NCH_2CH_2), 29.9 (t, SCH_2CH_2), 34.0 (t, NCH_2), 47.6 (t, aromatic CH_2), 52.2 (t, SCH_2), 126.8–141.1 (aromatic).

General Procedure for Preparation of the Nickel Complexes. The dihydrochloride salt of the macrocycle was dissolved in water, neutralized with sodium bicarbonate, and extracted into chloroform. The chloroform was then removed on a rotary evaporator to yield the macrocycle as an oil. The oil (10^{-3} mol) in methanol or butanol was added slowly to a stirred, hot solution of nickel chloride (10^{-3} mol) in methanol or butanol. The solution was stirred for 5 min and then concentrated whereupon the complex separated. The product was washed with methanol or butanol and then with ether; it was dried over P_2O_5 in a vacuum. All complexes were obtained in greater than 70% yield. Anal. Calcd for $Ni_2(14\text{-}MAC)Cl_4 \cdot {}^1/_2BuOH$, $C_{20}H_{27}N_2S_2O_{0.5}$: C, 38.3; H, 4.3; N, 4.5; Ni, 18.7. Found: C, 38.0; H, 4.5; N, 4.5; Ni, 18.4. IR: broad ν_{OH} at ~3300 cm^{-1}. Anal. Calcd for $Ni(15\text{-}MAC)Cl_2 \cdot {}^1/_2H_2O$, $C_{19}H_{25}Cl_2N_2S_2O_{0.5}$: C, 47.2; H, 5.2; N, 5.8; Ni, 12.2. Found: C, 47.2; H, 5.3; N, 5.8; Ni, 11.9. IR: broad ν_{OH} at ~3300 cm^{-1}. Anal. Calcd for $Ni(16\text{-}MAC)Cl_2 \cdot H_2O$, $C_{20}H_{28}Cl_2N_2S_2O$: C, 47.5; H, 5.6; N, 5.5; Ni, 11.6. Found: C, 47.5; H, 5.4; N, 5.4; Ni, 11.6. IR: broad ν_{OH} at ~3300 cm^{-1}.

Results and Discussion

Although one of the dialdehyde precursors for the new macrocyclic ligands has been prepared previously in low yield,[13] the dialdehyde synthesis outlined in the Experimental Section is superior and leads to a considerably higher yield. From the respective dialdehydes, the new macrocycles were produced by nontemplate condensation of the appropriate diamine followed by sodium borohydride reduction of the cyclic diimine to yield the corresponding cyclic diamines **2**–**4**.

Nickel(II) complexes of these S_2N_2-donor macrocycles were prepared by addition of a stoichiometric amount of nickel chloride to solutions of the respective ligands in hot methanol or butanol. Physical data (Table I) suggest that the nickel complexes of **3** and **4** have an octahedral geometry related to that of their O_2N_2 analogues;[7,16] crystal structure determinations involving the nickel halide complexes of the 14-,[17] 15-,[9] and 16-membered[18] O_2N_2 macrocycles indicate that each complex has a trans pseudooctahedral geometry. However, reaction of nickel chloride with **2** yields a purple microcrystalline solid which exhibits a nickel:macrocycle ratio of 2:1. In the absence of an X-ray diffraction investigation, details of the structure of this complex must remain uncertain.

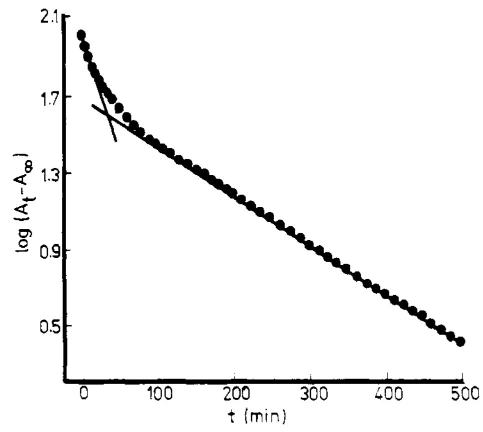

Figure 1. Dissociation of $Ni(15\text{-}MAC)Cl_2$ in 1 M HCl at 25 °C plotted according to first-order kinetics.

Table II. Dissociation of $Ni(15\text{-}MAC)Cl_2$ in Aqueous HCl

[H$^+$], M	$10^4k_1^{25}$,^{a,b} s^{-1}	$10^5k_2^{25}$,^{a,b} s^{-1}
1.0	(7.2 ± 0.2)	(9.4 ± 0.2)
1.0^{c}	5.5	7.9
0.05^{d}	(7.2 ± 0.2)	(9.2 ± 0.1)
9.0 × 10^{-3} ^{d}	(7.7 ± 0.1)	(9.7 ± 0.7)
ΔH, kJ mol^{-1} ^{e,f}	92 ± 5	98 ± 5
ΔS, J K^{-1} mol^{-1}	−36 ± 8	−42 ± 9

[a] Errors represent the average deviation from the mean of at least two individual determinations. [b] Complex concentration 1.5 × 10^{-3} M. [c] 90% D_2O. [d] Ionic strength = 1.0 (KCl). [e] Determined from least-squares fits to the Eyring equation with use of data from six temperatures over the range 20–47 °C. [f] Errors represent three standard deviations.

Kinetics of Dissociation of $Ni(15\text{-}MAC)Cl_2$. As a continuation of our kinetic studies involving nickel complexes of the O_2N_2-donor macrocycles of type **1**,[8] the dissociation of $Ni(15\text{-}MAC)Cl_2$ in hydrochloric acid has been investigated. The reaction was followed spectrophotometrically, and the data were plotted according to first-order kinetics (Figure 1). Because of low solubilities coupled with small absorbance changes on reaction, the nickel complexes of **2** and **4** were found to be unsuitable for kinetic study.

The observed behavior for $Ni(15\text{-}MAC)Cl_2$ is in accord with the existence of two consecutive first-order reactions, with the

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(16) The solid-state visible spectrum of $Ni(15\text{-}MAC)Cl_2 \cdot {}^1/_2H_2O$ and of its O_2N_2 macrocyclic analogue both indicate distorted structures with symmetries lower than O_h; the limited resolution together with the complexity of these spectra make ligand field comparisons difficult. In contrast, the corresponding dithiocyanato complexes both give spectra typical of O_h symmetry. For $Ni(15\text{-}MAC)NCS_2$, a 10*Dq* value of 10 750 cm^{-1} was obtained whereas the value for the analogous O_2N_2 macrocyclic complex is 10 310 cm^{-1} (from ref 7). The order thus reflects the expected ligand field strengths (namely, thioether sulfur greater than ether oxygen). The nickel dithiocyanate complex of 15-MAC was prepared from nickel thiocyanate and macrocycle by a similar procedure to that used for the corresponding dichloro complex. Anal. Calcd for $Ni(15\text{-}MAC)NCS_2$: C, 48.6; H, 4.7; N, 10.8. Found: C, 48.6; H, 4.9; N, 10.9.

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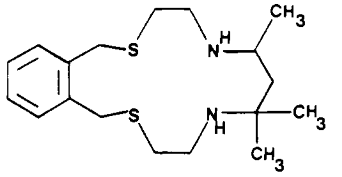
second being slower than the first. Although other interpretations are possible, in view of the known stepwise dissociation of other macrocyclic systems,[19] the present data were treated according to

$$[\mathrm{Ni(MAC)}]^{2+} \xrightarrow{k_1} \text{intermediate} \xrightarrow{k_2} \text{products}$$

By means of a computer fit, values of k_1 and k_2 which best reproduced the observed absorbance values were obtained (Table II). The value of k_1 is about 1 order of magnitude greater than k_2, and both constants are considerably smaller than the first-order dissociation rate constant (3.5×10^{-3} s^{-1}) determined previously, under identical conditions, for the nickel complex of the analogous O_2N_2 macrocycle (**1**, $n = 3$ and $m = 2$).[8] Both steps show no significant acid dependence, and both are accelerated in the presence of acetate[20]—results which once again parallel observations made for the previously studied O_2N_2 system. The small difference between the values of k_1 (and also of k_2) which were obtained in H_2O and D_2O are also in accord with the acid independence of the dissociation.

The similarity of the $\Delta H^{\ddagger}$ values obtained for the two steps (Table II) suggests that they reflect successive removal of similar donor atoms from the nickel. The observed acid independence of both steps together with the markedly slower dissociation rates relative to that of the analogous O_2N_2-donor complex further suggest that it is the dissociation of the sulfur donor atoms which are observed in the present study.

A recent study[6] of the kinetics of dissociation of the related nickel complex of **5** yielded a single first-order dissociation



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constant of 2.8×10^{-5} s^{-1} (25 °C; $I = 0.5$). Once again the dissociation was found to be acid independent, and thus this appears to be a characteristic of the dissociation of nickel complexes of the X_2N_2-donor (X = O, S) macrocycles studied so far.[6,8]

Acknowledgment. We acknowledge the Australian Institute for Nuclear Science and Engineering for a travel grant and the Australian Research Grants Committee for support. We thank Dr. J. T. Baker of the Roche Research Institute of Marine Pharmacology, Sydney, Australia, for assistance.

Registry No. **2**·2HCl, 76124-43-1; **3**·2HCl, 76124-44-2; **4**·2HCl, 76124-45-3; Ni_2(14-MAC)Cl_4, 76299-34-8; Ni(15-MAC)Cl_2, 76137-02-5; Ni(16-MAC)Cl_2, 76137-03-6; 1,4-bis(2-benzyl alcohol)-1,4-dithiabutane, 76124-46-4; 1,5-bis(2-benzyl alcohol)-1,5-dithiapentane, 76124-47-5; 1,4-bis(2-formylphenyl)-1,4-dithiabutane, 25676-67-9; 1,5-bis(2-formylphenyl)-1,5-dithiabutane, 76124-48-6; 1,4-bis(2-carboxyphenyl)1,4-dithiabutane, 52961-83-8; 1,5-bis(2-carboxyphenyl)-1,5-dithiapentane, 76124-49-7; 1,2-diaminoethane, 107-15-3; 1,3-diaminopropane, 109-76-2.

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(20) Previously, we have shown[8] that the presence of acetate ion leads to an increase in the first-order dissociation rate of the nickel complex of the O_2N_2 macrocyclic ligand (**1**, $n = 3$ and $m = 2$). During the present study we have carried out a parallel investigation in which the dissociation of the analogous complex of ligand **3** in acetic acid (1 M)/sodium acetate (1 M) buffer (pH 4.5—the same conditions as used for the previous study) was followed. As before, enhanced dissociation was observed; under these conditions the respective values for k_1 and k_2 are $(2.7 \pm 0.2) \times 10^{-3}$ s^{-1} and $(5.6 \pm 0.1) \times 10^{-4}$ s^{-1}. However, as discussed in ref 8, the mechanism of the rate enhancement by acetate remains uncertain.

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Crystal and Molecular Structure of $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$. An Example of Highly Unsymmetrical Bonding of an η^3-Benzyl Ligand

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and B. C. Schardt

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$(\eta^3\text{-L})$Co(phosphite)$_3$ complexes (L = allyl, cyclooctenyl, benzyl) have been shown to be catalyst precursors for the homogeneous hydrogenation of aromatic hydrocarbons.[2] Although the catalytic chemistry and spectroscopic properties of this series of compounds have been studied extensively, their structural chemistry has not been described. We now wish to report the crystal and molecular structure of $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$, a compound of particular interest because it possesses a simple benzyl ligand in the relatively unusual η^3 bonding mode.[3]

Experimental Section

A. Collection of X-ray Diffraction Data. Red-brown needles of $(\eta^3\text{-}CH_2C_6H_5)Co[P(OCH_3)_3]_3$[3e] were grown from a saturated methanol solution at −40 °C. A crystal of dimensions 0.40 × 0.23 × 0.10 mm was mounted in a thin-walled, 0.3-mm glass capillary under argon. Preliminary precession photographs indicated $2/m$ Laue symmetry with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with the monoclinic space group $P2_1/c$.

The crystal was mounted on a Nonius CAD-4 four-circle, κ-geometry diffractometer automated by a PDP8-E minicomputer and Enraf-Nonius software. A preliminary orientation matrix was determined by searching reciprocal space in the region near $2\theta = 12°$ and indexing the reflections found.

Accurate cell dimensions and orientation matrix were determined by centering 24 reflections (6 sets of 4 symmetry-related reflections) with 2θ values between 23.64 and 24.98°. Table I gives the derived crystal parameters and details of the data collection procedure.

All data reduction and structure refinement was done on the University of California at Berkeley Chemistry Department X-Ray Facility's PDP 11/60 computer using local modifications of the Enraf-Nonius structure determination package.[4] The 3534 reflections collected were reduced to structure factor amplitudes and their esd's by corrections for Lorentz and polarization effects, scan time, and background. Inspection of the standard reflections showed a maximum decay of 7.2% in F_o. All intensities were scaled accordingly. Observations of the intensities of several reflections [(051), (061), (020)] near $\chi = 90°$ at 10° increments of rotation around the diffraction vectors showed a maximum variation of ~8%. Absorption corrections were performed with use of the calculated absorption coefficient ($\mu = 9.9$ cm^{-1}), the Miller indices of the faces bounding the crystal [(021), (0,−2,−1), (102), (−1,0,−2), (1,0,−2), (−1,0,2)], and the dimensions of these faces. Reflections equivalent by Laue symmetry were averaged and those corresponding to systematic absences were deleted to yield

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