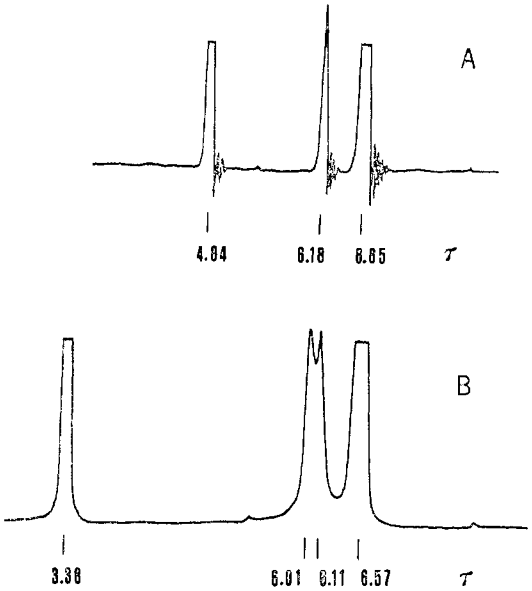

Figure 3.—Proton magnetic resonance spectra: A, $Na_2[(Mo_6Cl_8)(OCH_3)_6]$, 40.9% solution in methanol; B, $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$, 58.8% solution in methanol.

shows proton magnetic resonance spectra of both $Na_2[(Mo_6Cl_8)(OCH_3)_6]$ and $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ in methanol as a solvent. The sharp peak at 6.18 ppm in the spectrum of the first compound is due to the protons of the ligand methoxide ions, the strong peak at 6.65 ppm, to the methyl protons of the methanol, and the other, at 4.84 ppm, to the hydroxyl protons of the methanol. The area of the peak at 6.18 ppm corresponds to six methoxy groups. This estimate is made possible by the high concentration of the solution, which allows a fairly accurate comparison of the areas of the peaks. Furthermore, the fact that the peak is so sharp clearly indicates equivalency among the methoxide ions. A similar spectrum is given by a solution of $Na_2[(Mo_6Br_8)(OCH_3)_6]$ in methanol.

In the spectrum of the solution of $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ the peak due to the methoxy groups of the compound has become a well-defined doublet with maxima at 6.01 and 6.11 ppm. The splitting leaves little doubt about the existence in the molecule of two types of methoxy groups, in complete agreement with the proposed structure.

The peaks at 6.57 and 3.38 ppm are due to the methyl and hydroxyl protons of the solvent, respectively. The areas under the peaks of the doublet cannot be determined separately because of overlap; however, the total area of the doublet corresponds to 14 methoxy groups. There are indications that the maximum at 6.01 ppm may be due to the ligand methoxide ions. When traces of water are added to the methanol solution of $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$, the peak at 6.01 ppm slowly decreases in intensity and eventually disappears, leaving the peak at 6.11 ppm unchanged. The ligand methoxide ions presumably are the first to be hydrolyzed, with consequent weakening and eventual disappearance of their pmr signal.

Acknowledgments.—The partial support of this work by the Office of Naval Research is gratefully acknowledged. The magnetic balance at Villanova University was kindly made available to us by Professor A. J. Leffler, H. D. McLaughlin assisted in much of the experimental work, and our analytical department performed the elemental analyses, conductivity measurements, and molecular weight determinations. We are particularly indebted to Dr. G. R. Leader for his assistance with the proton nmr portion of this work.

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Complexes of Nickel(II) with Cyclic Tetradentate Schiff Bases Derived from 2-Mercaptoaniline[1]

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The synthesis, electrical conductivity, and electronic spectra are described for a number of complexes of nickel(II) with the new cyclic planar tetradentate ligands S,S′-*o*-xylyl-2,3-butanedione bis(2-mercaptoanil) and S,S′-*o*-xylyl-1,2-cyclohexanedione bis(2-mercaptoanil) and the related noncyclic ligand S,S′-dibenzyl-2,3-butanedione bis(2-mercaptoanil). The complexes are prepared by the action of α,α'-dibromo-*o*-xylene or α-bromotoluene on the nickel(II) complexes of the Schiff base of the appropriate α-diketone and 2-mercaptoaniline. Bromide, iodide, and thiocyanate salts have been isolated. All of the complexes show high-spin magnetic moments and are 1:1 electrolytes in acetonitrile. Their electronic spectra have been assigned on the basis of a model of tetragonally distorted octahedral symmetry, and the ligand field strengths of the new ligands and the tetragonal splitting parameters have been estimated and compared with those of related ligands.

Introduction

A survey[2] of complexes of nickel(II) with cyclic tetradentate ligands reveals that the great majority involve ligands which have either a double negative charge or no charge at all, giving neutral or doubly positively charged complex species, respectively. In the latter class, the charge on the cation usually is compensated by two mononegative anions which may, or may not, be coordinated. Considerable interest is attached to the

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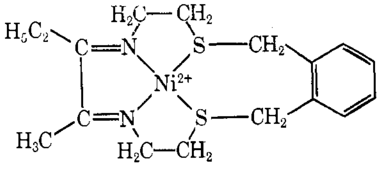
[1] Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967.

[2] D. H. Busch, *Helv. Chim. Acta*, Fasciculus Extraordinarius Alfred Werner, 174 (1967).

properties of these compounds, as both high-spin triplet and low-spin singlet complexes are formed, each with characteristic magnetic moment and electronic spectrum. Moreover, for a number of ligands there exist one or more nickel(II) complexes in which the singlet and triplet states coexist, commonly in thermal equilibrium.

Many of these cyclic ligands involve four nitrogen atoms as donors.[3-5] In contrast to the abundant information on these systems there has been much less work performed on complexes containing other combinations of donor atoms. Complexes of ligands having two nitrogen and two sulfur donor atoms have been prepared,[6,7] but little information is available as to their physical properties. The only well-studied example of this type of complex is (S,S′-*o*-xylyl-2,3-pentanedione bis(mercaptoethylimine))nickel(II), $Ni(PEX)^{2+}$ (I), which is synthesized[8] by the alkylation of the nickel complex of the Schiff base of 2,3-pentanedione and β-mercaptoethylamine, Ni(PE). The magnetic properties, electrical conductivity, and electronic spectra have been studied[8,9] for a series of complexes of the type $Ni(PEX)Y_2$, where Y^- was ClO_4^-, I^-, Br^-, Cl^-, N_3^-, and NCS^-. Similar but noncyclic complexes $Ni(PEB)Br_2$ and $Ni(PEM)I_2$ (II) are produced[10] by the reaction of Ni(PE) with α-bromotoluene and iodomethane, respectively.



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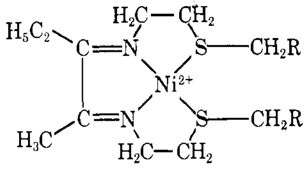
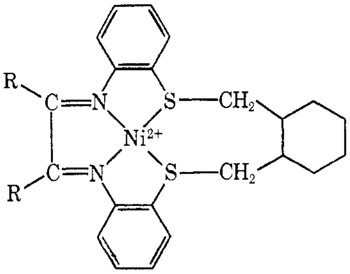


II

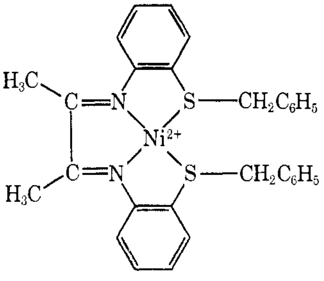
$Ni(PEM)^{2+}$, R = H

$Ni(PEB)^{2+}$, $R = C_6H_5$

In this paper we report the synthesis of complexes of nickel(II) with two new, related, cyclic, tetradentate ligands, (S,S′-*o*-xylyl-2,3-butanedione bis(2-mercaptoanil))nickel(II), $Ni(BMAX)^{2+}$ (IIIa), and (S,S′-*o*-xylyl-1,2-cyclohexanedione bis(2-mercaptoanil))nickel(II), $Ni(CMAX)^{2+}$ (IIIb), and also with a new noncyclic ligand, (S,S′-dibenzyl-2,3-butanedione bis(2-mercaptoanil))nickel(II), $Ni(BMAB)^{2+}$ (IV). A study of the physical properties of the iodide, bromide, and thiocyanate derivatives of these species has permitted more extensive comparisons between complexes with four nitrogen donor atoms and those with two nitrogen and two sulfur donor atoms, between complexes of cyclic planar tetradentate ligands and those of related noncyclic ligands, and, also, between those containing aromatic thioether groups and their aliphatic analogs.



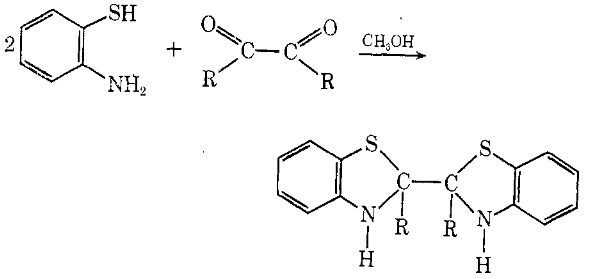
IIIa, $R = CH_3$
b, $R = {}^1/_2C_4H_8$



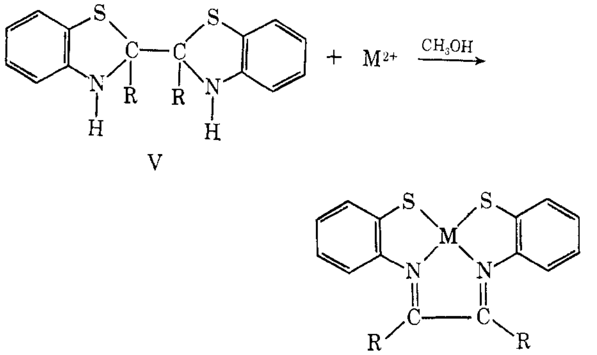
IV

Results and Discussion

To prepare the new cations $Ni(BMAX)^{2+}$, $Ni(CMAX)^{2+}$, and $Ni(BMAB)^{2+}$, it was first necessary to prepare the complexes of nickel(II) with the Schiff bases of 2,3-butanedione and 1,2-cyclohexanedione with 2-mercaptoaniline. This was achieved by the procedure devised by Jadamus, *et al.*,[11] for the synthesis of similar complexes of zinc and cadmium, eq 1 and 2.



(1)



(2)

V

VI

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[3] N. F. Curtis and D. A. House, *J. Chem. Soc., A*, 537 (1967).

[4] J. L. Karn and D. H. Busch, *Nature*, **211**, 160 (1966).

[5] G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4834 (1964).

[6] F. L. Urbach and D. H. Busch, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., 1966, No. H95.

[7] N. B. Egen and R. A. Krause, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966, No. N52.

[8] M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964).

[9] G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, **5**, 2114 (1966).

[10] D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Am. Chem. Soc.*, **86**, 3642 (1964).

[11] H. Jadamus, Q. Fernando, and H. Freiser, *ibid.*, **86**, 3056 (1964); E. Bayer and E. Breitmaier, *Chem. Ber.*, **101**, 1579 (1968).

Table I

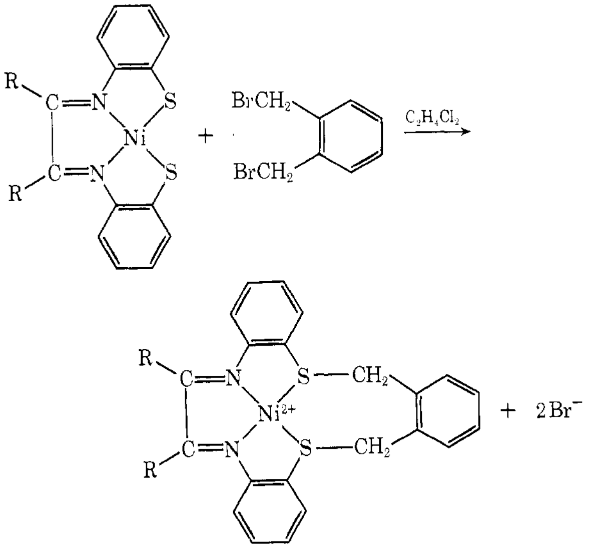
Analyses and Properties of Alkylated Complexes

	% calcd					% found					λ,[a] ohm⁻¹	μ,
Compound	C	H	N	S	Y	C	H	N	S	Y	cm²	BM
Ni(BMAX)Br_2	46.41	3.57	4.51	10.32	25.73	46.09	3.63	4.60	9.77	25.32	159	3.27[b]
Ni(CMAX)Br_2	48.25	3.74	4.33	9.91	24.70	47.98	3.49	4.31	9.37	24.59	148	3.17[c]
Ni(BMAX)I_2	40.31	3.10	3.92	8.97	35.50	39.92	3.05	3.72	8.73	35.92	166	2.92[b]
Ni(BMAX)$(NCS)_2$	53.71	3.81	9.64	22.75		53.71	3.86	9.74	21.62		135	3.12[b]
Ni(CMAX)$(NCS)_2$	55.73	4.01	9.29	21.25		55.59	3.95	9.28	20.83		143	3.24[c]
Ni(BMAB)Br_2	51.53	4.03	4.01	9.17	22.86	51.32	4.09	3.96	8.78	22.78	152	3.13[b]

[a] 10^{-3} *M* solutions in acetonitrile at 24°. [b] Determined by the Gouy method. [c] Determined by the Faraday method.

The reactions were originally used to prepare zinc and cadmium complexes of the Schiff bases derived from glyoxal, GMA (VI, R = H), and 2,3-butanedione, BMA (VI, R = CH_3). During this work these preparations of the zinc complexes were successfully repeated, and the method was extended to the synthesis of complexes of nickel(II), Ni(GMA) and Ni(BMA), and of iron(II), Fe(GMA). While this research was in progress, Ni(GMA) was reported elsewhere.[12] The isolation of Fe(GMA) required the addition of sodium acetate to the solution produced by reaction 2. It was also possible to prepare the nickel(II) complex derived from 1,2-cyclohexanedione, Ni(CMA) (VI, R = $^1/_2C_4H_8$), but attempts to prepare complexes from 2,3-pentanedione or 2,3-octanedione were frustrated by failure to synthesize the intermediate thiazoline (V), the only identified sulfur-containing product from reaction 1 being the disulfide of 2-mercaptoaniline.

Ni(BMA) and Ni(CMA) were converted to Ni(BMAX)Br_2 and Ni(CMAX)Br_2 by treatment with the difunctional alkylating agent α,α′-dibromo-*o*-xylene



(3)

The reaction of α,α′-dibromo-*o*-xylene with coordinated mercaptide groups to give a cyclic ligand was originated by Thompson[8] in his synthesis of the Ni(PEX)$^{2+}$ cation (I). It has been shown[13] that the rate of macrocyclic ring closure is fast compared with the rate of reaction of the first sulfur atom of Ni(PE) with the alkylating agent, but the formation of the Ni(BMAX)$^{2+}$ and Ni(CMAX)$^{2+}$ cations is probably a more complicated process. The 20% yields are much lower than expected, and the precipitated bromides are greatly contaminated with Ni$(NH_2C_6H_4S)_2$. Moreover, it must be emphasized that the successful preparation of these complexes requires strict adherence to particular reaction conditions. The only suitable solvent is 1,2-dichloroethane, decomposition occuring in, for example, N,N-dimethylformamide. It is also necessary to conduct the reaction at room temperature, and to use a large (tenfold) excess of the alkylating agent. The products are also decomposed by hydroxylic solvents such as alcohols and by small quantities of water in other solvents. The complexes are soluble without decomposition only in dry acetonitrile. Apart from Ni$(NH_2C_6H_4S)_2$ the side products were not identified, but it seems probably that some polymerization or partial alkylation is involved. These vicissitudes have frustrated attempts to prepare alkylated derivatives of Ni(GMA) or of the zinc or iron complexes. This sensitivity to solvents contrasts with the stability of Ni(PEX)$^{2+}$, for which many derivatives could be prepared by metatheses in methanol.[8] Here, restriction to acetonitrile has limited the metathetical products to the iodide and thiocyanate derivatives.

Reactions with monofunctional alkylating agents were preformed in the same manner as those with α,α′-dibromo-*o*-xylene, but a pure product was isolated only from the reaction of α-bromotoluene with Ni(BMA).

The analytical results for the alkylated products are given in Table I. The compounds were insufficiently soluble in nonionizing solvents to allow the determination of molecular weights.

The infrared spectra of these complexes were similar over the range 4000–400 cm⁻¹ but consist mostly of bands due to *ortho*-disubstituted benzene rings. The thiocyanate complexes showed the expected strong band due to the asymmetric stretching mode at 2080 cm⁻¹, but this is known[14,15] to be an unreliable guide to the mode of coordination of the thiocyanate ion. The more useful but weak symmetric stretching and deformation modes could not be distinguished from the strong benzenoid absorptions.

Table I also lists the magnetic moments of these complexes at room temperature. All of the values are consistent with high-spin, six-coordinate nickel(II) with the possible exception of Ni(BMAX)I_2, for which a slightly lower moment of 2.92 BM was found. By

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(12) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965).

(13) E. L. Blinn and D. H. Busch, *Inorg. Chem.*, **7**, 820 (1968).

(14) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(15) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

analogy with the $Ni(PEX)^{2+}$ complexes,[9] the iodide would be the most likely complex to show a thermally accessible singlet ground state, but there can be only a small contribution, if any, from this source in $Ni(BMAX)I_2$. The existence of triplet ground states for the halide complexes suggests that these macrocyclic ligands exhibit comparatively weak ligand fields, as other series of tetradentate macrocyclic complexes often have at least one diamagnetic member.[2] This conclusion is supported quantitatively by the electronic spectra (*vide infra*).

Molar conductivities for the complexes at 10^{-3} *M* concentrations in acetonitrile are given in Table I. The average value of 150 ohm^{-1} cm^2 shows that the complexes are dissociated, but to distinguish between 1:1 and 1:2 ionization the variation of conductivity with concentration was studied, as first performed by Feltham and Hayter[16] for aqueous solution and more recently applied to solutions in acetonitrile.[17]

The results of this investigation are shown in Table II. The equivalent conductivity λ_E is related to the equivalent conductivity at zero concentration $\lambda_E{}^0$ and concentration c by the Onsager equation

$$\lambda_E = \lambda_E{}^0 + A\sqrt{c}$$

TABLE II

ELECTRICAL CONDUCTIVITY PARAMETERS FOR $Ni(BMAX)Y_2$ IN ACETONITRILE AT 25°

Y	$\lambda_E{}^0$	A_{exptl}	$A_{1:1}$	$A_{1:2}$
Br	175	395	360	780
I	169	425	355	770
NCS	150	370	340	750

The constant A can be calculated[18] and has widely different values for 1:1 and 1:2 electrolytes. The results show that the $Ni(BMAX)Y_2$ complexes are 1:1 electrolytes in acetonitrile, probably having a solvent molecule coordinated to the vacated axial position. It is interesting to note that $Ni(PEX)Br_2$ is a 1:1 electrolyte in methanol and a 1:2 electrolyte in water but gives intermediate values in N,N-dimethylformamide.[8]

The dissociation of the complexes in the only suitable solvent, acetonitrile, demanded that the electronic spectra be recorded in the solid state, and the diffuse reflectance spectra so obtained are reported in Table III. The spectra of the $Ni(CMAX)Y_2$ complexes are similar to those of $Ni(BMAX)Y_2$. Some bands of higher intensity, presumably of the charge-transfer type, were observed above 19,000 cm^{-1}, but these will not be discussed here. Most of the bands are not at all well resolved, and the values given should not be regarded as precise.

TABLE III

ELECTRONIC SPECTRA[a]

Compound	ν_1	ν_2	ν_3	ν_4
$Ni(BMAX)I_2$	7800	9300	11,000	15,400
$Ni(BMAX)Br_2$	7700	9300	10,900	15,600
$Ni(BMAX)(NCS)_2$	7600	9300	10,600	14,300
$Ni(BMAB)Br_2$	7700	9500	12,300	15,100

[a] All values in cm^{-1}.

The electronic spectra of complexes of nickel(II) with planar cyclic tetradentates have been most useful in assessing the electronic structure of tetragonally distorted octahedral complexes. The treatment to be followed here has been adapted[2,9,19] to nickel(II) from the original model for cobalt(III) and chromium(III) species having D_{4h} and C_{4v} symmetry.[20] On this basis the following assignments are made: ν_1, $^3B_{1g} \rightarrow {}^3E_g{}^a$; ν_2, $^3B_{1g} \rightarrow {}^3B_{2g}$.

The energy of ν_2 (the $^3B_{1g} \rightarrow {}^3B_{2g}$ transition) is $10Dq^{xy}$ and should be unaffected by different axial ligands. The energy of ν_1 is given by $\nu_1 = 10Dq - 35/4Dt$, and this band provides a measure of the tetragonal distortion of the complexes.

Assignment of the other two bands in the spectra is not so simple. They cannot both be due to transitions to components of the $^3T_{1g}(F)$ state, since these would not be so far apart. Comparison of the relative intensities of the ν_2 and ν_3, ν_4 transitions in the $Ni(PEX)Y_2$ complexes suggests that band IV involves the transition to $^3T_{1g}(F)$ and that band III may be the $^3B_{1g} \rightarrow {}^1E_g$ transition, which should occur at about this position.

The indifferent resolution shown in the spectra does not justify extensive data reduction but a few simple deductions can be made. Thus, Dt can be calculated for the various axial ligands and is found to be about 180 cm^{-1} (Table IV). Similar results were found for the paramagnetic halides of $Ni(PEX)Y_2$ and of $Ni(PEB)Br_2$,[9,10] but $Ni(PEX)(NCS)_2$ gave the unusual value of -124 cm^{-1}, indicating NCS^- to be a stronger ligand than the macrocycle. Our value for NCS^- is positive, and, in fact, NCS^- appears to be comparable to Br^- in ligand field strength. This suggests sulfur coordination but our infrared data are not adequate to check this possibility.

TABLE IV

LIGAND FIELD PARAMETERS FOR $NiLBr_2$

L	Dq^{xy}, cm^{-1}	Dt, cm^{-1}	Ref
BMAX	930	180	This work
BMAB	950	210	This work
PEX	1062	187	10
PEB	1210	194	11

Also, it appears that the ligand field strengths of BMAX and BMAB are lower than those of PEX and PEB. This can be attributed to the poorer donor abilities of aromatic amines and thioethers than their aliphatic analogs. This results in BMAX having the lowest Dq of any cyclic tetradentate ligand for which nickel(II) complexes have been characterized so far.

Finally, it seems that cyclization has an adverse effect on the strengths of the donors in these planar tetradentate ligands. This effect is shown by comparing Dq

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(16) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(17) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

(18) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 128.

(19) J. L. Karn, Ph.D. Thesis, The Ohio State University, 1966.

(20) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **5**, 709, 1524 (1965).

values for BMAX and BMAB and, more strikingly, for PEX and PEB. Indeed, PEB shows a *Dq* value more comparable with those for cyclic tetramines. Decreases in *Dq* values upon cyclization are also found for tetramine complexes of nickel(II)[19] and cobalt(III).[21]

Parenthetically, it should be noted that the assignments given in ref 10 for the electronic spectra of Ni(PEB)Br$_2$ and Ni(PEM)I$_2$ are erroneous. The corrected assignments are: ν_1, $^3E_g \leftarrow {}^3B_{1g}$; ν_2, $^3B_{2g} \leftarrow {}^3B_{1g}$; and ν_3, $^3A_{2g}$, $^3E_g \leftarrow {}^3B_{1g}$.

Experimental Section

Materials.—1,2-Dichloroethane was dried over 5 Å molecular sieve and acetonitrile was dried with calcium hydride and phosphorus pentoxide.[22] Other materials were of reagent grade whenever possible and were not purified before use. 2,2-Bisbenzthiazoline and 2,2′-dimethyl-2,2′-bisbenzthiazoline were made by the method of Jadamus, *et al.*[11]

2,2′-(1,2-Cyclohexyl)-2,2′-bisbenzthiazoline.—The method of Jadamus, *et al.*,[11] for the dimethyl analog was followed. The product was recrystallized from acetone. A 24% yield was obtained. *Anal.* Calcd for $C_{18}H_{18}N_2S_2$: C, 66.22; H, 5.56; N, 8.58; S, 19.64. Found: C, 66.30; H, 5.79; N, 8.26; S, 18.42.

(Glyoxal bis(2-mercaptoanil))nickel(II), Ni(GMA).—The procedure of Jadamus, *et al.*,[11] for the cadmium analog was followed. A 50% yield of the deep green Ni(GMA) was obtained. *Anal.* Calcd for $C_{14}H_{10}N_2NiS_2$: C, 51.07; H, 3.06; N, 8.54; Ni, 17.84; S, 19.49. Found: C, 50.97; H, 3.01; N, 8.77; Ni, 18.51; S, 19.36.

(2,3-Butanedione bis(2-mercaptoanil))nickel(II), Ni(BMA).—The procedure of Jadamus, *et al.*,[11] for Cd(GMA) was followed. A 63% yield of the deep green Ni(BMA) was obtained. *Anal.* Calcd for $C_{16}H_{14}N_2NiS_2$: C, 53.79; H, 3.95; N, 7.86; Ni, 16.43; S, 17.97. Found: C, 53.51; H, 3.96; N, 7.66; Ni, 16.60; S, 17.79.

(1,2-Cyclohexanedione bis(2-mercaptoanil))nickel(II), Ni(CMA)—The procedure of Jadamus, *et al.*,[11] for Cd(GMA) was used, giving a 73% yield of the deep green Ni(CMA). *Anal.* Calcd for $C_{18}N_{16}N_2NiS_2$: C, 56.42; H, 4.21; N, 7.31; N, 15.32; S, 16.74. Found: C, 56.20; H, 4.23; N, 7.10; Ni, 15.57; S, 16.59.

(Glyoxal bis(2-mercaptoanil))iron(II), Fe(GMA).—This reaction was performed in a nitrogen-filled glove box using deaerated solvents. To a refluxing solution of 2,2′-bisbenzthiazoline (5.0 g, 0.018 mol) in methanol (600 ml) was added one of $FeCl_2 \cdot 4H_2O$ (3.66 g, 0.018 mol) in methanol (70 ml). The mixture was refluxed for 1 hr and to it was added solid sodium acetate (4.0 g, 0.05 mol). The black microcrystalline precipitate of Fe(GMA) which formed at once was filtered from the hot solution, washed with hot methanol and with ether, and dried at 80° *in vacuo*. A 58% yield was obtained. *Anal.* Calcd for $C_{14}H_{10}FeN_2S_2$: C, 51.54; H, 3.09; Fe, 17.12; N, 8.59; S, 19.66. Found: C, 51.20; H, 3.21; Fe, 17.90; N, 8.71; S, 20.36.

Dibromo(S,S′-*o*-xylyl-2,3-butanedione bis(2-mercaptoanil))nickel(II), Ni(BMAX)Br$_2$.—To a stirred slurry of Ni(BMA) (6.1 g, 0.017 mol) in 1,2-dichloroethane (400 ml) was added a solution of α,α'-dibromo-*o*-xylene (46 g, 0.17 mol) in 1,2-dichloroethane (100 ml). After 15 hr the light green precipitate was filtered and washed with ether. The solid was Soxhlet extracted with acetonitrile, the extract was evaporated at room temperature in a rotary evaporator, and the residual green-brown Ni(BMAX)Br$_2$ was washed with ether and dried *in vacuo* over P_2O_5. A yield of 2.22 g (21%) was given. The analyses of this and the other alkylation products are shown in Table I.

Dibromo(S,S′-*o*-xylyl-1,2-cyclohexanedione bis(2-mercaptoanil))nickel(II), Ni(CMAX)Br$_2$.—To a stirred slurry of Ni(CMA) (3.8 g, 0.01 mol) in 1,2-dichloroethane (400 ml) was added a solution of α,α'-dibromo-*o*-xylene (26 g, 0.10 mol) in 1,2-dichloroethane (100 ml). After 15 hr the light green solution was filtered from the precipitated $Ni(NH_2C_6H_4S)_2$ and evaporated at room temperature in a rotary evaporator. The excess alkylating agent was removed by washing with ether, and the remaining green-brown Ni(CMAX)Br$_2$ was purified by Soxhlet extraction with acetonitrile, concentration of the extract, precipitation with ether, and drying *in vacuo* over P_2O_5. A yield of 1.54 g (24%) was obtained. Analytical data are in Table I.

Dibromo(S,S′-dibenzyl-2,3-butanedione bis(2-mercaptoanil))nickel(II), Ni(BMAB)Br$_2$.—To a stirred slurry of Ni(BMA) (1.19 g, 0.0033 mol) in 1,2-dichloroethane (100 ml) was added α-bromotoluene (11.4 g, 0.066 mol). After 15 hr the green precipitate was filtered, the solution was concentrated to an oil at room temperature in a rotary evaporator, and more solid was precipitated by the addition of ether. The two fractions were combined, extracted with 1,2-dichloroethane, and reprecipitated with ether after concentration on a rotary evaporator. The green-brown Ni(BMAB)Br$_2$ (1.53 g, 65%) was washed with ether and dried *in vacuo* over P_2O_5. Analytical data are in Table I.

Iodo and Thiocyanato Derivatives of Ni(BMAX)$^{2+}$ and Ni(CMAX)$^{2+}$.—Saturated solutions in acetonitrile of stoichiometric proportions of the complex bromide and appropriate sodium salt were mixed and the precipitated sodium bromide was removed by filtration. The solutions were concentrated to oils on a rotary evaporator and the products were precipitated with ether. The compounds were purified by reprecipitation with ether from concentrated solutions in acetonitrile, washed with ether, and dried *in vacuo* over P_2O_5. Analyses of these products are given in Table I.

Physical Measurements.—Microanalyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were obtained from a Perkin-Elmer Model 337 spectrophotometer. Magnetic moments were determined on Gouy and Faraday balances calibrated with $HgCo(NCS)_4$. Electrical conductivities were determined with an Industrial Instruments, Inc., Model RC 16B bridge. Diffuse reflectance spectra were recorded on a Cary Model 14 spectrophotometer, using mixtures of the complexes and the appropriate sodium salt. $MgCO_3$ was the reference material.

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[21] E. Ochiai and D. H. Busch, unpublished observations.

[22] J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padinamabhan, *Anal. Chem.*, **34**, 1139 (1962).