well as the cis isomer. They also consider square-pyramidal transition states which are accessible by somewhat more extensive rearrangement than that permitted in Figure 9e. For the most part, kinetic results for Co(mhd)$_3$ and Co(bzac)$_3$ are similar, and both studies point to a bond-rupture mechanism involving a high percentage of axial trigonal-bipyramidal transition states.

Acknowledgments. The support of this research by National Science Foundation Grant No. GP-16280 is gratefully acknowledged. A. G. thanks the American Association of University Women for a fellowship. We also thank Professor R. H. Holm for a preprint of ref 33 and Professor J. W. Faller for some helpful comments on the evaluation of the microscopic rate constants.

Iron(II), Cobalt(II), Nickel(II), and Zinc(II) Complexes of a Series of New Macrocyclic Sexadentate Ligands

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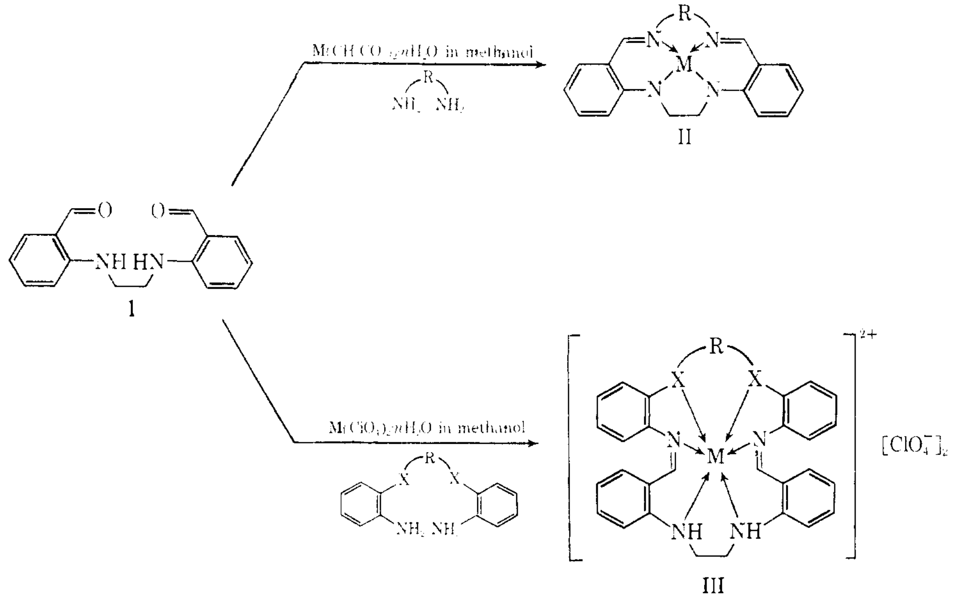
Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received February 19, 1970*

Abstract: The reaction *in situ* of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione, the appropriate metal(II) perchlorate, and the appropriate diamine containing two additional donor sites (*e.g.*, 1,2-bis(2-aminophenylthio)ethane) in methanol gives metal complexes of the type [M(L)](ClO$_4$)$_2$·CH$_3$OH, where L represents a macrocyclic sexadentate ligand (*e.g.*, 15,18-dithia-1,5,8,12-tetraaza-3,4:9,10:13,14:19,20-tetrabenzocycloeicosane-1,11-diene (N$_4$S$_2$)). The physical properties of the complexes are consistent with a formulation with all six donor sites in the macrocycle bonded to a single metal ion. This arrangement was confirmed for the [Fe(N$_4$S$_2$)]$^{2+}$ cation by a single-crystal X-ray structure determination, which also established which of the three possible geometric isomers is present.

When 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (I) is condensed with various diamines in the presence of methanolic solutions of metal(II) acetates, the quadridentate macrocyclic planar complexes (II) are obtained (reaction 1, R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, and o-C_6H_4).[1] We wish to report here the use of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (I) to synthesize the sexadentate macrocyclic ligand complexes (III) according to the scheme outlined in reaction 2. In these complexes (III), the ligands are uncharged and closely resemble the macrocycle (IV) reported recently by Busch and Lindoy.[2] Transition metal complexes of four other cyclic sexadentate ligands have been reported recently. The ligands V,[3] VI,[4]



(1)

(2)

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* Address correspondence to this author at the University of California, Irvine, Calif.

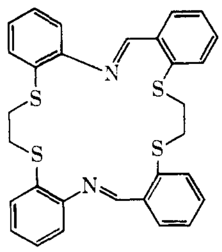
(1) M. Green and P. A. Tasker, *Chem. Commun.*, 518 (1968); M. Green and P. A. Tasker, in preparation.

(2) L. F. Lindoy and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4690 (1969).

(3) D. St. C. Black and I. A. McLean, *Chem. Commun.*, 1004 (1968).

(4) J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 592 (1964).

and VII[5] will be expected to be considerably more flexible than those discussed in this work, while the "cage" system[6] of VIII will be expected to be much more rigid.



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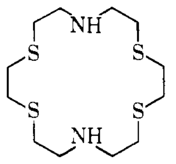

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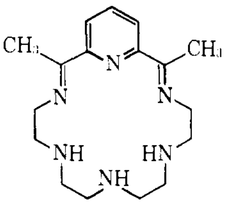

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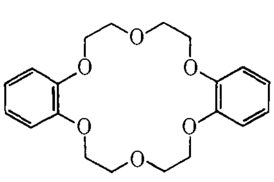
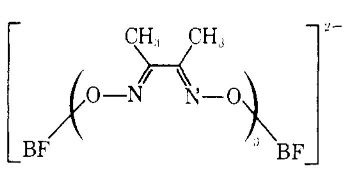


VII



VIII

Experimental Section

The synthesis of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione has been described previously.[1] 1,2-Di(*o*-aminophenylthio)ethane and 1,2-di(*o*-nitrophenoxy)ethane were prepared by the method of Venanzi, *et al.*[7] Analyses were performed by MicroTech Laboratories, Skokie, Ill., and by Dr. A. Bernhardt in Mülheim. Electronic absorption spectra were recorded with a Cary Model 14M recording spectrophotometer and infrared spectra as Nujol and hexachlorobutadiene mulls on a Beckman IR10 spectrophotometer. Magnetic measurements were made on Cahn microbalance using the Faraday method, and nuclear magnetic resonance spectra were recorded on a Varian A60 instrument, using tetramethylsilane as internal standard.

1,2-Di(*o*-nitrophenylamino)ethane. 1-Chloro-2-nitrobenzene (200 g) was heated with 1,2-diaminoethane (26 ml) so that the 1,2-diaminoethane refluxed gently. The mixture was stirred vigorously, and when the 1,2-diaminoethane had all reacted, the heating was reduced to keep the mass molten for a further 4 hr. The melt was poured into ethanol (500 ml). The resulting solid was washed with diethyl ether (300 ml), benzene (300 ml), and 1 *N* sodium methoxide solution (100 ml), and recrystallized from 1,2-dichloroethane to give 1,2-di(*o*-nitrophenylamino)ethane (31 g, 27%) as bright orange needles, mp 192–194°.

Anal. Calcd for $C_{14}H_{14}N_4O_4$: C, 55.63; H, 4.67; N, 18.53; O, 21.17. Found: C, 55.36; H, 4.68; N, 18.56; O, 21.13.

1,2-Di(*o*-aminophenylamino)ethane (enN_4). 1,2-Di(*o*-nitrophenylamino)ethane (10 g) in ethanol (300 ml) was heated under reflux with 5% palladium–carbon (0.5 g). Hydrazine hydrate (20 ml) was added in 5-ml portions, and the mixture was refluxed until the solution had become colorless. After filtration the solution was evaporated to dryness and crystallized from hot ethanol under nitrogen when 1,2-di(*o*-aminophenylamino)ethane (6.5 g, 81%) was obtained as white needles: mp 100–104°; nmr (pyridine-d_5 solution) τ 2.97–3.42 (aromatics, complex), 5.28 (NH_2, broad), 6.57 (methylene, singlet).

Anal. Calcd for $C_{14}H_{18}N_4$: C, 69.39; H, 7.48; N, 23.12. Found: C, 69.59; H, 7.53; N, 22.94.

1,3-Di(*o*-nitrophenylamino)propane. 1-Chloro-2-nitrobenzene (20 g) was heated with 1,3-diaminopropane (5 ml) in refluxing bis-(2-methoxyethyl) ether (20 ml) for 30 min. The resulting orange solid was washed with diethyl ether (20 ml), benzene (20 ml), and 1 *N* sodium methoxide solution (20 ml), and recrystallized from chloroform to give bright orange prisms of 1,3-di(*o*-nitrophenylamino)propane (4.4 g, 39%): mp 144°; nmr (dimethyl sulfoxide-d_6) τ 1.67–3.67 (aromatic, complex), 6.50 (α-methylene, quartet, $J_{\alpha CH_2, \beta CH_2} = 7$, $J_{\alpha CH_2, NH} = 7$ cps, 8.00 (β-methylene, quintet, $J = 7$ cps).

Anal. Calcd for $C_{15}H_6N_4O_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 56.67; H, 5.13; N, 17.61.

1,3-Di(*o*-aminophenylamino)propane (tnN_4). 1,3-Di(*o*-nitrophenylamino)ethane (10 g) was reduced with hydrazine and 5% palladium–carbon as described in the synthesis of 1,2-di(*o*-aminophenylamino)ethane above. 1,3-Di(*o*-aminophenylamino)propane (6.1 g, 75%) was obtained as fine white needles, mp 80°, on recrstallization from 50% aqueous ethanol: nmr (chloroform-*d*) τ 3.17–3.50 (aromatic, complex), 6.63 (NH_2, singlet), 6.78 (α-methylene, triplet, $J = 6.5$ cps), 8.08 (β-methylene, quintet, $J = 6.5$ cps).

Anal. Calcd for $C_{15}H_{20}N_4$: C, 70.28; H, 7.86; N, 21.85. Found: C, 70.33; H, 7.92; N, 21.78.

1,2-Di(*o*-aminophenoxy)ethane (N_2O_2). 1,2-Di(*o*-nitrophenoxy)ethane (5 g) was reduced with hydrazine and 5% palladium–carbon as was described above in the synthesis of 1,2-di(*o*-diaminophenylamino)ethane. 1,2-Di(*o*-aminophenoxy)ethane (3 g, 74%) was crystallized from ethanol as white plates: mp 130–132° (lit.[7] mp 129–132°); nmr (dimethyl sulfoxide-d_6 solution) τ 3.0–3.6 (aromatic, complex), 5.40 (NH_2, broad), 5.67 (methylene, singlet).

Preparation of the Metal Complexes of Table I. 4,7-Diaza-2,3:8,9-dibenzodecane-1,10-dione (500 mg), an equimolar quantity of the required diamine, and a slight excess of the required metal(II) perchlorate hydrate were heated in refluxing methanol (40 ml) for 24 hr. The metal complexes were collected and washed with a little methanol and diethyl ether. Only the zinc(II) complexes required purification before analysis. These were precipitated from an acetone solution by the addition of diethyl ether.

15,18-Dioxa-1,5-8,12-tetraaza-3,4:9,10:13,14:19,20-tetrabenzocycloeicosane-1,11-diene (N_4O_2). 4,7-Diaza-2,3:8,9-dibenzodecane-1,10-dione (200 mg) and 1,2-di(*o*-aminophenoxy)ethane (200 mg) were heated in refluxing methanol (20 ml) with zinc(II) perchlorate (300 mg) for 6 hr. The fine yellow needles of 15,18-dioxa-1,5,8,12-tetraaza-3,4:9,10:13,14:19,20-tetrabenzocycloeicosane (178 mg, 55%) were collected and recrystallized from pyridine to give bright yellow needles: mp 212–213°; nmr (pyridine-d_5 + little dimethyl sulfoxide-d_6) τ −0.22 (NH, broad), 1.24 (methine, singlet), 2.25–3.40 (aromatics, complex), 5.42 ("phenoxy" methylene, singlet), 6.24 ("anilino" methylene, complex).

Anal. Calcd for $C_{30}H_{28}N_4O_2$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.50; H, 5.86; N, 11.71.

15,18-Dithia-1,5,8,12-tetraaza-3,4:9,10:13,14:19,20-tetrabenzocycloeicosane-1,11-diene (N_4S_2). The zinc(II) complex (50 mg) of this ligand (see above) was treated with pyridine (1 ml), and warmed for a few minutes at 100°. Chloroform (1 ml) was added and the mixture filtered. The filtrate was heated to remove the chloroform, and then added slowly to water with stirring. 15,18-Dithia-1,5-8,12-tetraaza-3,4:9,10:13,14:19,20-tetrabenzocycloeicosane-1,11-diene (20 mg, 63%) was obtained as a bright yellow powder, mp 125–130°; nmr (pyridine-d_5) τ 1.45 (methine, singlet), 2.34–3.50 (aromatics, complex), 4.0 (NH, broad), 6.17 ("anilino" methylene, complex), 6.63 ("thioether" methylene, singlet).

Anal. Calcd for $C_{30}H_{28}N_4S_2$: C, 70.83; H, 5.55; N, 11.01; S, 12.61. Found: C, 70.93; H, 5.35; N, 10.72; S, 12.23.

X-Ray Diffraction Experimental Procedures. Crystals of $[Fe(N_4S_2)](ClO_4)_2 \cdot CH_3OH$ were obtained from the reaction mixture. The crystals belong to the space group $P2_1/n$ with cell constants $a = 17.469 \pm 0.005$, $b = 11.538 \pm 0.003$, $c = 16.979 \pm 0.004$ Å, $\gamma = 98.13 + 0.01°$, which were determined by a least-squares refinement on 31 θ_{hkl}'s taken with a GE single-crystal orienter using Cu Kα radiation. The observed density, obtained by flotation in a CH_3I–benzene mixture, is 1.49 g/cm³. The calculated density for four molecules per cell is 1.55 g/cm³. This discrepancy may be due in part to diffusion of the lattice methanol into the flotation mixture.

A crystal with dimensions 0.25 × 0.10 × 0.50 mm³ was mounted and the data were obtained with Mo Kα silicon monochromated X-rays, employing a Pailred automatic diffractometer.

Peaks with $\theta \leq 20°$ were collected in layers with fixed *l* values, and were scanned at a rate of 1°/min with scan widths of 3°. Owing to limitations of instrument geometry, on each layer ten reflections with low *h* and *k* values could not be reached automatically. These data were obtained by manual centering of the scan range on the peak required, and then scanning through the peak in the same way as for the automatic collection. However, when a peak had insufficient intensity to allow such manual centering of the scan it was not measured. In this way 68 reflections were excluded from the possible data set of reflections with $\theta < 20°$. Play in the automatic

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(5) A. C. L. Su and J. F. Weiher, *Inorg. Chem.*, 7, 176 (1968).

(6) D. R. Boston and N. J. Rose, *J. Amer. Chem. Soc.*, 90, 6859 (1968).

(7) R. D. Cannon, B. Chiswell, and L. M. Venanzi, *J. Chem. Soc. A*, 1277 (1967).

Table I. Elemental Analyses and Effective Magnetic Moments for the Complexes

Compound	Color	μ_{eff},[a] BM	Temp, °K	% C		% H		% N		% S	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Zn(N_4S_2)](ClO_4)_2 \cdot CH_3OH$	Off white			46.25	45.93	4.00	3.61	6.96	6.96	7.96	7.76
$[Zn(enN_6)](ClO_4)_2 \cdot CH_3OH$	White			48.29	48.19	4.44	4.05	10.90	11.24		
$[Zn(tnN_6)](ClO_4)_2$	White			49.41	50.00	4.28	4.38	11.16	11.40		
$[Ni(N_4S_2)](ClO_4)_2 \cdot CH_3OH$	Orange	3.17	292	46.70	46.82	4.04	3.79	7.01	7.31	8.03	8.32
$[Ni(N_4O_2)](ClO_4)_2 \cdot CH_3OH$	Yellow	3.18	295	48.59	48.24	4.21	4.00	7.31	7.19		
$[Co(N_4S_2)](ClO_4)_2 \cdot CH_3OH$	Red-brown	1.97	291	46.62	46.63	4.04	3.54	7.02	7.27	8.03	8.47
$[Fe(N_4S_2)](ClO_4)_2 \cdot CH_3OH$	Deep blue	0.87[b]	292	46.81	46.99	4.06	4.28	7.04	7.88	8.06	8.88
$[Fe(enN_6)](ClO_4)_2 \cdot CH_3OH$	Deep blue	0.66[b]	295	48.91	49.49	4.54	4.09	11.04	11.88		
$[Fe(tnN_6)](ClO_4)_2$	Deep blue	0.82[b]	295	50.09	50.24	4.34	4.13	11.30	11.32		

[a] After correction for ligand susceptibility. [b] Temperature-independent paramagnetism has been predicted and found to be in this range for similar low-spin systems: E. Sinn, *Inorg. Chim. Acta*, **1**, 11 (1969).

drive system of the diffractometer unfortunately caused certain reflections to be "missed" during the data collection. This problem is discussed below.

The 2,2,0 reflection was monitored after every layer, and the average of the monitor was 9408 counts with an average deviation of ±48 and a maximum deviation of 200 from the average. The overall stability of the system is judged to be better than ±1% from these observations.

The data reduction program calculated the Lorentz-polarization factors and a counting error $\Delta I/I = (T + t^2B)^{1/2}/[T - tB]$ (B is the sum of the background counts taken at both ends of the scan, T is the total number of counts of the peak (ω scan), and $t = t_T/t_B$, where t_T and t_B are total times for the scan and for the background, respectively). Fifty-one peaks for which the ratio of the backgrounds exceeded 1.5, and all peaks with counting errors >0.5 were not accepted in the final F_o list of 1311 nonzero peaks which were used in the refinement.

No correction for absorption was applied to the data. The structure was solved by application of Patterson and Fourier analysis, and refined with full-matrix least squares, employing a weighting scheme with $w = 1/\sigma^2(F)$, where $\sigma = -0.084F_o + 261.1$ if $F_o < 1871$ and $\sigma = 0.067F_o - 20.71$ if $F_o > 1871$ (F's in electrons × 41.21). This weighting scheme was derived by plotting ΔF against F_o in the final stages of refinement and using this curve, defining σ so that $w\Delta F$ is independent of F_o. The final refinement included anisotropic thermal parameters for the iron, sulfur, and chlorine atoms, while isotropic parameters were used for the remaining atoms. Hydrogen atom positions were calculated by assuming C–H and N–H bond lengths of 1.08 and 1.02 Å, respectively. The hydrogen atoms were included in the least squares without refinement of their parameters. Both the real and imaginary parts of the scattering factors[8] were included in the refinement.

The final R factors[9] for the 1311 reflections used in the refinement are $R_1 = 10.9\%$ and $R_2 = 10.8\%$.

When all the reflections except the systematic absences (a total of 3263) are included in the calculations of the R factors, the values become $R_1 = 28.1\%$ and $R_2 = 19.7\%$. The observed and calculated data are shown in Table V.[10] It was found that several "zero" reflections (with counting errors >0.5) are calculated far above the limits of detection. The most serious of these are the low-angle reflections −3,1,0, 0,2,0, −2,2,0, −3,1,1, 0,2,1, −2,2,1, and −3,1,2. Since six of these (−3,1,0, 0,2,0, −2,2,0, −3,1,1, 0,2,1, and −2,2,1) appear on $h,k,0$ and h,k,l layer precession photographs as strong reflections, it appears that they were missed by the automatic diffractometer during the data collection.

This missing of reflections was due to some wear on the Pailred X–Y drive, causing a large error in low-angle reflections. The crystal also showed unusually high backgrounds, as can be seen by the intensities that were obtained for the extinctions. The photographs clearly show the extinctions as having zero intensity and it can only be concluded that the general background scattering was high in the crystal.

The atomic parameters are listed in Table III, and some of the bond distances are listed in Table IV. An ORTEP drawing of the cation is shown as structure XVII.

Results and Discussion

Physical measurements on the neutral quadridentate complexes I have suggested that the arrangement of the four donor atoms about the metal is planar, even when the bridging group is long (*e.g.*, R = $-(CH_2)_4-$) and some of the strain in the ligand could be relieved by a "tetrahedral" distortion. The complexes II show little tendency to increase their coordination number beyond four on solution in coordinating solvents such as pyridine. Both of these observations are consistent with the strong planar ligand field which would be expected to be developed by the dianionic "N_4" ligand.

If the length of R is increased sufficiently, the square planarity of the N_4 field must be destroyed. If at the same time donor groups are located in R, a multidentate macrocyclic ligand might be produced with the additional donor atoms coordinated to the metal. To further decrease the ligand field produced by the four nitrogens and hence enhance the possibility of further coordination, conditions should be chosen to decrease the chance of loss of protons from the ligands (*e.g.*, metal(II) perchlorates should be used as the sources of metal ions rather than metal(II) acetates).

Under these conditions the sexadentate macrocyclic ligand complexes III were produced in a single step as outlined in reaction 2.

In the absence of metal salts, the reactions of the dialdehyde I and the quadridentate diamines produced no detectable amount of the four ligands IX–XII. Thus it appears that the metal ions have some catalytic or "template" activity in the formation of these ligands.

The complexes prepared in this study are listed in Table I. The elemental analyses are consistent with empirical formulas for the metal complexes of the cyclic ligands IX–XII. Formulation as metal complexes of the sexadentate cyclic monomeric ligands, rather than of polymeric ligands, is supported by synthesis of the complexes from the characterized preformed ligands (see below), and by the X-ray structure of the compound $[Fe(N_4S_2)](ClO_4)_2 \cdot CH_3OH$.

When acetone solutions of the complexes are treated with pyridine, the cyclic ligands are liberated. The rates of dissociation vary considerably with the nature of the ligand and the complexed metal. The nickel(II) complex $[Ni(N_4S_2)](ClO_4)_2$ appears to give an inter-

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(8) All atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. III, C. H. MacGillavry, G. D. Rieck, and K. Lonsdale, Ed., Kynoch Press, Birmingham, England, 1962, pp 210–215.

(9) $R_1 = \Sigma\{||F_o| - |F_c||\}/\Sigma\{|F_o|\}$, $R_2 = (\Sigma\{||F_o| - |F_c||\}^2/\Sigma w|F_o|^2)^{1/2}$.

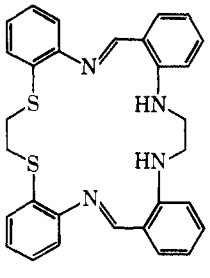
(10) This table has been deposited as Document No. NAPS-01213 with the ASIS National Auxiliary Publication Service c/o CCM Information Corp., 909 3rd Ave., New York, N.Y. 10022. A copy may be secured by citing the document number and by remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

Table II. Electronic Absorption Spectra of the Complexes in Acetone Solution

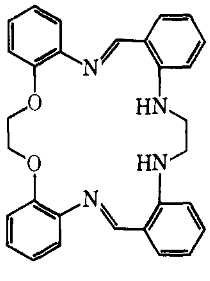
Complex	λ_{max}, cm^{-1}	ϵ	λ_{max}, cm^{-1}	ϵ	λ_{max}, cm^{-1}	ϵ	λ_{max}, cm^{-1}	ϵ
$[Fe(N_4S_2)](ClO_4)_2 \cdot CH_3OH$	11,200 (sh)[a]	19	15,700	3670	18,100	3600	25,100	1100
$[Fe(enN_6)](ClO_4)_2 \cdot CH_3OH$	14,800	6650	16,100 (sh)	5280	21,000	1400	25,600 (sh)	2170
$[Fe(tnN_6)](ClO_4)_2$	11,600 (sh)	1500	14,100	5900	16,400	5700	21,400 (sh)	6200
					22,200 (sh)	5800	24,300 (sh)	4800
$[Co(N_4S_2)](ClO_4)_2 \cdot CH_3OH$	14,800	1220	19,000	5860				
$[Ni(N_4S_2)](ClO_4)_2 \cdot CH_3OH$	12,600	46	19,000 (sh)	300	22,700 (sh)	1050	25,000 (h)	1580
$[Ni(N_4O_2)](ClO_4)_2 \cdot CH_3OH$	12,100	30	20,600 (sh)	400				

[a] sh, shoulder.

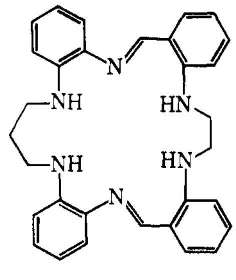
mediate before liberating the cyclic ligand IX. These reactions are presently being studied in this laboratory.



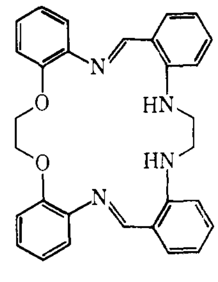
IX, N_4S_2



X, enN_6



XI, tnN_6



XII, N_4O_2

When the zinc complexes are dissolved in dimethyl sulfoxide-d_6 or pyridine-d_5 the solutions show proton magnetic resonances characteristic of the free ligands.

The iron(II) and zinc(II) complexes of the ligand N_4O_2, XII, could not be synthesized under conditions which were effective for the other complexes of Table I. The weak donor capacity of the "ether-type" oxygen atoms (III, X = O) in comparison with sulfur and nitrogen atoms (III, X = S or NH) may be responsible for this effect.

The Free Ligands. Besides being obtained by decomposition of the complexes, the free cyclic ligands were by-products when the condensation (reaction 2) was performed in the presence of zinc(II) perchlorate (free N_4O_2 (XII) was the exclusive product under these conditions). Peaks corresponding to the molecular ions of IX–XII were obtained in the mass spectra of these materials, which support formulation of the ligands as the cyclic monomeric 1:1 condensation products IX–XII of reaction 2.

Physical Properties of the Complexes. Preliminary identification of the metal complexes was made on the basis of their infrared spectra. The strong band at 1660 cm^{-1} characteristic of the aldehyde groups in I is absent in the products of reaction 2, and a band appears in the region 1600–1620 cm^{-1} which can be assigned to the azomethine stretch, by analogy with other workers' results.[11] The azomethine stretch occurs at slightly lower energy in the complexes than in the free ligands, but the shifts are small, and thus an analysis of the variation of bonding with the nature of the ligand and metal ion is inappropriate.

Formulation of the complexes with methanol of crystallization is supported by the broad absorptions found at 3550 cm^{-1}. Methanol of solvation was confirmed in the crystal structure of $[Fe(N_4S_2)](ClO_4)_2 \cdot CH_3OH$, which has one methanol molecule per iron atom in the crystal lattice. The lack of appreciable splitting of the strong perchlorate bands (1080–1087 cm^{-1}) supports[12] structure in which the perchlorate ions are not coordinated to the metal ions.

The room-temperature effective magnetic moments are listed in Table I. The iron(II) complexes have moments consistent with their formulation as low-spin octahedral d^6 systems. The cobalt complex $[Co(N_4S_2)](ClO_4)_2 \cdot CH_3OH$ is also low spin. If coordination of all six donor atoms is assumed, then this compound falls into the fairly unusual[13] group of low-spin octahedral cobalt(II) complexes. In this regard it is of interest to note that the cobalt(II) complex of the "N_2S_4" ligand (IV) is also low spin,[2] and that several of the other octahedral low-spin cobalt(II) complexes reported[14] involve (linear) sexadentate ligands containing nitrogen and sulfur donors.

The paramagnetism of the nickel(II) complexes is typical of octahedral high-spin nickel(II) compounds, which have room-temperature effective magnetic moments in the range 2.9–3.3 BM.[15]

Electronic Spectra. The spectra were recorded as acetone solutions and as Nujol mulls. The bands in the visible region occurred in similar positions for both the mull and solution spectra, suggesting that the coordination geometry is the same in the solid state and in acetone solutions. Addition of strong donors or solution in good donor solvents caused immediate changes in the spectra and resulted in eventual decomposition of the complexes, giving solutions showing the strong characteristic ligand absorptions at 26,000–25,000 cm^{-1}.

The iron(II) complexes show strong bands in the region 19,000–14,000 cm^{-1} (see Table II), and these are presumably responsible for the blue and blue-violet colors. The positions and shapes of the peaks do not resemble the other typical deep blue octahedral

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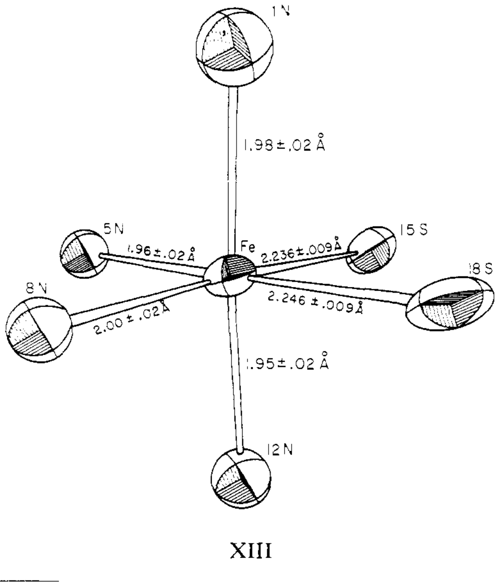
low-spin iron(II) complexes of the "terpyridyl-type" ligands which show[16] two bands in the region 22,500–15,000 cm^{-1}. However, the terpyridyl-type ligands have only five-membered chelate rings, and this is probably responsible for the difference from the iron(II) complexes of IX–XI (see Table III), rather than distortions from octahedral geometry in the latter. The d–d transitions are mainly obscured by the strong charge-transfer bands in the visible regions, and so assignments which would allow a comparison of the ligand fields of the various ligands are not possible for the iron complexes.

The complex $[Co(N_4S_2)](ClO_4)_2 \cdot CH_3OH$ shows a band at 14,800 cm^{-1} which is probably related to that reported[2] for the cobalt(II) complex of IV. This band may correspond to the $(^2T_{2g}, {}^2T_{1g} \leftarrow {}^2E_g)$ absorption for low-spin cobalt(II). The additional very weak absorption around 10,000 cm^{-1} which was reported[2] for the cobalt(II) complex of IV was not detected in the spectrum of $[Co(N_4S_2)](ClO_4)_2 \cdot CH_3OH$.

The nickel(II) complexes show spectra consistent with octahedral high-spin d^8 systems. Since the lowest energy (ν_1) bands due to the absorption $(^3T_{2g} \leftarrow {}^3A_{2g})$ show no sign of splitting, an O_h symmetry model was used for interpreting the spectra. On this basis it appears that the ligands IX, XII, and IV produce ligand fields ($10Dq$ = 12,600, 12,100, and 12,700 cm^{-1}, respectively) close to the value[17] for the tris(2,2′-dipyridyl) system ($10Dq$ = 12,650 cm^{-1}). If the shoulder at 19,000 cm^{-1} in the spectrum of $[Ni(N_4S_2)](ClO_4)_2 \cdot CH_3OH$ is assigned to the $\nu_2(^3T_{1g}(F) \leftarrow {}^3A_{2g})$ band the energy of the ν_3 transition $(^3T_{1g}(P) \leftarrow {}^3A_{2g})$ can be calculated as 29,600 cm^{-1}, which is in a region obscured by solvent absorption. The calculated energy for the $(^3T_{1g}(P) \leftarrow {}^3A_{2g})$ transition gives $\beta(B_{complex}/B_{free\ ion}) = 0.68$, which is close to the value determined for the $[Ni(dipy)_3]^{2+}$ ion ($\beta = 0.72$).

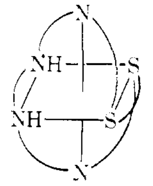
Coordination Geometry. The physical measurements described above suggest that the complexes of Table I have an octahedral arrangement of the six donor atoms of the macrocycles about a single metal ion. This type of structure was confirmed by a single-crystal X-ray structure performed on the iron(II) complex $[Fe(N_4S_2)](ClO_4)_2 \cdot CH_3OH$. The iron coordination sphere is shown in XIII. A slight distortion from octahedral geometry is apparent, allowing the iron–sulfur bonds to be longer than the iron–nitrogen bonds. This distortion and the longer bridges between the N_1 and N_5 and N_8 and N_{12} donors than those between the N_1 and S_{18} and N_{12} and S_{15} donors probably are responsible for the nonlinearity of the N_1–F–N_{12} axis in the octahedron (angle 175.0 ± 1.0°).



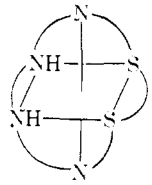
XIII

Assuming that adjacent donors in the macrocycle cannot coordinate in trans octahedral positions allows only three possible geometric isomers: XIV, XV, and XVI, for the complex $[Fe(N_4S_2)](ClO_4)_2 \cdot CH_3OH$. Each of these isomers is capable of showing optical isomerism. No attempt has been made to resolve the compounds of Table I into their optical isomers, and this may prove to be a difficult task in view of lability of the complexes.

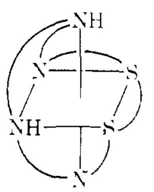
The structure determination shows that the idealized configuration XIV is applicable in the complex [Fe-



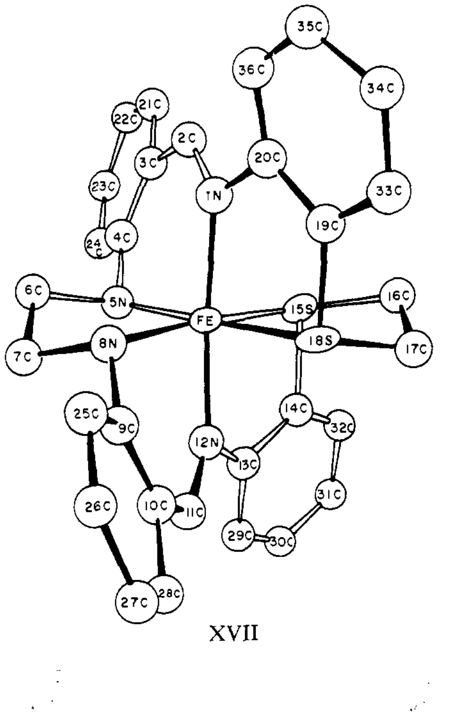
XIV



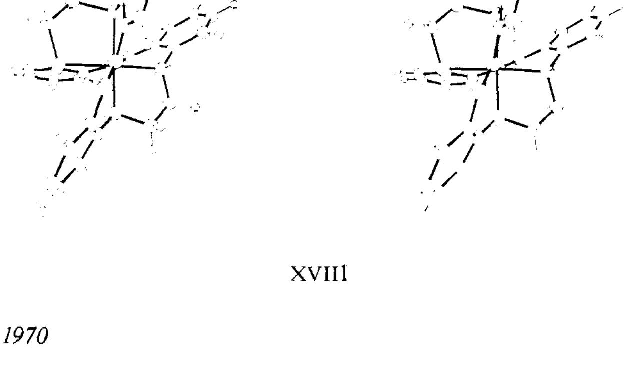
XV



XVI



XVII



XVIII

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(17) A. B. P. Lever "Physical Inorganic Chemistry," M. F. Lappert, Ed., Elsevier, Amsterdam, 1968, p 336.

Table III. Atomic Parameters for $[Fe(N_4S_2)](ClO_4)_2 \cdot CH_3OH$

Atom[a]	$x(\sigma)^b \times 10^4$	$y(\sigma) \times 10^4$	$z(\sigma) \times 10^4$	$B(\sigma)^c \times 10^2$
Fe	3880 (2)	1251 (4)	1866 (2)	*d*
N_1	2918 (13)	511 (21)	1339 (15)	320 (54)
C_2	2752 (14)	−617 (24)	1195 (16)	239 (56)
C_3	3231 (14)	−1498 (23)	1431 (16)	216 (54)
C_4	3850 (15)	−1310 (22)	1962 (17)	275 (60)
N_5	4026 (12)	−220 (17)	2378 (12)	195 (49)
C_6	3511 (17)	−422 (12)	3108 (21)	428 (68)
C_7	3532 (18)	739 (28)	3515 (19)	393 (69)
N_8	3344 (12)	1593 (18)	2866 (12)	194 (47)
C_9	3485 (16)	2821 (24)	3176 (18)	347 (65)
C_{10}	4250 (16)	3362 (25)	3151 (19)	367 (65)
C_{11}	4903 (14)	2945 (22)	2844 (15)	201 (55)
N_{12}	4818 (12)	2098 (19)	2329 (13)	238 (48)
C_{13}	5548 (16)	1884 (24)	1981 (18)	322 (65)
C_{14}	5515 (15)	1495 (22)	1215 (16)	236 (59)
S_{15}	4588 (4)	882 (7)	823 (5)	*d*
C_{16}	4372 (16)	1907 (25)	102 (18)	335 (68)
C_{17}	4281 (16)	3087 (24)	446 (17)	315 (67)
S_{18}	3654 (4)	2936 (6)	1309 (5)	*d*
C_{19}	2718 (14)	2440 (23)	927 (15)	230 (64)
C_{20}	2411 (14)	1251 (22)	1000 (15)	202 (54)
C_{21}	3081 (16)	−2590 (27)	1016 (17)	347 (66)
C_{22}	3484 (20)	−3502 (30)	1146 (21)	517 (81)
C_{23}	4134 (18)	−3321 (28)	1628 (20)	477 (80)
C_{24}	4304 (17)	−2241 (26)	2043 (18)	385 (70)
C_{25}	2843 (16)	3294 (27)	3450 (17)	364 (71)
C_{26}	3024 (19)	4416 (30)	3744 (20)	509 (85)
C_{27}	3775 (20)	5072 (30)	3775 (20)	508 (73)
C_{28}	4382 (16)	4522 (25)	3506 (17)	301 (60)
C_{29}	6319 (15)	2203 (22)	2282 (16)	205 (52)
C_{30}	6946 (15)	2067 (23)	1819 (19)	316 (60)
C_{31}	6901 (19)	1765 (29)	1062 (20)	495 (79)
C_{32}	6168 (18)	1408 (27)	744 (19)	408 (68)
C_{33}	2257 (15)	3189 (23)	606 (16)	246 (57)
C_{34}	1484 (17)	2776 (25)	426 (17)	326 (67)
C_{35}	1192 (19)	1612 (31)	590 (20)	500 (83)
C_{36}	1654 (16)	877 (25)	874 (17)	300 (64)
Cl_1	1200 (5)	443 (8)	3391 (5)	*d*
O_1Cl_1	1660 (14)	247 (21)	2755 (15)	633 (59)
O_2Cl_1	468 (16)	−247 (24)	3341 (16)	805 (75)
O_3Cl_1	1123 (14)	1614 (23)	3449 (15)	687 (63)
O_4Cl_1	1588 (23)	135 (35)	4083 (26)	1370 (105)
Cl_2	5862 (5)	1869 (8)	4822 (6)	*d*
O_1Cl_2	5519 (22)	1960 (33)	5538 (24)	1273 (104)
O_2Cl_2	6320 (19)	999 (29)	4741 (20)	1044 (91)
O_3Cl_2	6186 (22)	2925 (35)	4574 (24)	1285 (109)
O_4Cl_2	5211 (26)	1500 (37)	4414 (27)	1523 (128)
$O_{methanol}$	518 (14)	4649 (20)	1885 (16)	659 (59)
$C_{methanol}$	1188 (26)	4200 (35)	2270 (26)	821 (112)

[a] Atoms labeled as in XVII. [b] Fractional coordinates (standard deviations). [c] Thermal parameters (standard deviations). [d] Varied anisotropically

	$B_{11} \times 10^4$	$B_{22} \times 10^4$	$B_{33} \times 10^4$	$B_{12} \times 10^4$	$B_{13} \times 10^4$	$B_{23} \times 10^4$
Fe	13 (1)	35 (3)	16 (2)	−6 (2)	−4 (1)	3 (2)
S_{15}	24 (3)	46 (7)	21 (3)	−9 (4)	2 (3)	−2 (4)
S_{18}	23 (3)	30 (7)	30 (4)	−5 (4)	−8 (3)	−5 (4)
Cl_1	31 (4)	79 (8)	35 (4)	4 (4)	6 (3)	−11 (4)
Cl_2	27 (3)	76 (9)	38 (4)	0 (4)	0 (3)	7 (5)

Table IV. Bond Lengths in the 15,18-Dithia-1,5,8,12-tetraaza-3,4:9,10:13,14:19,20-tetrabenzocycloeicosane-1,11-diene Iron(II) Cation

Bond	Length, Å, ± σ	Bond	Length, Å, ± σ
Fe^a–N_1	1.99 ± 0.02[b]	S_{18}–C_{19}	1.78 ± 0.03
Fe–N_5	1.96 ± 0.02	C_{19}–C_{20}	1.41 ± 0.03
Fe–N_8	2.00 ± 0.02	C_{20}–N_1	1.43 ± 0.03
Fe–N_{12}	1.95 ± 0.02	C_3–C_{21}	1.43 ± 0.04
Fe–S_{15}	2.236 ± 0.009	C_{21}–C_{22}	1.36 ± 0.04
Fe–S_{18}	2.246 ± 0.009	C_{22}–C_{23}	1.39 ± 0.04
N_1–C_2	1.32 ± 0.03	C_{23}–C_{24}	1.43 ± 0.04
C_2–C_3	1.46 ± 0.04	C_{24}–C_4	1.43 ± 0.04
C_3–C_4	1.40 ± 0.03	C_9–C_{25}	1.40 ± 0.04
C_4–N_5	1.44 ± 0.03	C_{25}–C_{26}	1.38 ± 0.04
N_5–C_6	1.53 ± 0.04	C_{26}–C_{27}	1.42 ± 0.04
C_6–C_7	1.50 ± 0.04	C_{27}–C_{28}	1.39 ± 0.04
C_7–N_8	1.55 ± 0.04	C_{28}–C_{10}	1.46 ± 0.04
N_8–C_9	1.50 ± 0.03	C_{13}–C_{29}	1.44 ± 0.03
C_9–C_{10}	1.39 ± 0.03	C_{29}–C_{30}	1.38 ± 0.03
C_{10}–C_{11}	1.40 ± 0.04	C_{30}–C_{31}	1.33 ± 0.04
C_{11}–N_{12}	1.30 ± 0.03	C_{31}–C_{32}	1.40 ± 0.04
N_{12}–C_{13}	1.46 ± 0.03	C_{32}–C_{14}	1.41 ± 0.04
C_{13}–C_{14}	1.38 ± 0.04	C_{19}–C_{33}	1.37 ± 0.03
C_{14}–S_{15}	1.80 ± 0.03	C_{33}–C_{34}	1.40 ± 0.04
S_{15}–C_{16}	1.78 ± 0.03	C_{34}–C_{35}	1.40 ± 0.04
C_{16}–C_{17}	1.51 ± 0.04	C_{35}–C_{36}	1.34 ± 0.04
C_{17}–S_{18}	1.82 ± 0.03	C_{36}–C_{20}	1.35 ± 0.03

[a] Atoms labeled as in XVII. [b] Standard deviations.

$(N_4S_2)](ClO_4)_2 \cdot CH_3OH$. This isomer was predicted from models, since it allows the NH–N–S portion of the molecule to remain approximately planar, whereas XV and XVI do not. The stereoscopic view (XVIII) of the cation shows how the benzene rings bend away slightly from the planes containing the iron, "anilino" nitrogen, "imino" nitrogen, and sulfur atoms. The iron atom has been omitted from XVIII for clarity.

The ORTEP drawing (XVII) shows the labeling used for the atoms of the cation whose parameters are listed in Table III. The atoms of the perchlorate ions and the methanol solvate molecule are also included in Table III. One of the two perchlorate groups is considerably disordered, but the methanol solvate molecule occupies a fairly well-defined position.

The bond lengths of the $[Fe(N_4S_2)]$ cation are shown in Table IV and fall within the ranges expected for the various bonds involved.

Summary

The dialdehyde 4,7-dibenzo-2,3:8,9-dibenzo-1,10-dione (I) has proved to be a versatile reagent in the preparation of macrocyclic ligands. In addition to the series of sexadentate macrocycles reported here and the planar quadridentate macrocycles reported earlier,[1] a pentadentate system can be prepared from reaction of I with di(2-aminophenyl)amine. This system is presently being studied in this laboratory.

The lability of the complexes in which all six donor sites in the ligand are bonded to a single metal ion is at first sight surprising. Application of the so-called "macrocyclic effect"[18] may prove to be much less general than the "chelate effect" in predicting complex stabilities. The mechanism of dissociation of the complexes described in this paper is presently being studied and may throw some light on this situation.[19]

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(19) This work was partially supported by grants from the National Science Foundation and National Institutes of Health.