Intrusion of charge-transfer bands into the visible region renders the study of d–d transitions difficult. The most satisfactory reflectance spectrum was provided by $VO(ebas)_2$, and this can be attributed to the fact that the charge-transfer bands begin some 3–4 kK higher than do those in $VO(bas)_2$ and $VO(dbms)_2$. It seems clear that bands occurring at frequencies lower than 16.5 kK can be attributed to d–d transitions. Such bands are found in the reflectance spectra of $VO(ebas)_2$, $VO(bas)_2$, and $VO(dbms)_2$ at 15.4, 16.3, and 14.7, kK, respectively, and in solutions of 1,2-dibromoethane at 17.3 kK for $VO(ebas)_2$ and 16.7 kK (shoulder) for $VO(bas)_2$. The corresponding band for $VO(dbms)_2$ in 1,2-dibromoethane is totally obscured by a charge-transfer "tail." The reason that the bands are shifted to slightly higher energies in 1,2-dibromoethane is not clear, but it is not uncommon to find small differences between reflectance spectra and those measured in noncoordinating solvents.[14] An additional absorption is seen as a very poorly defined shoulder in 1,2-dibromoethane at approximately 10.5, 12.1, and 11.1 kK in the ebas, bas, and dbms complexes, respectively. Thus, the spectra are qualitatively similar to those of β-diketone complexes in the 10–20-kK region, except that only two bands are observable. Provisionally, the shoulders at 10.5–12.1 kK are assigned to transition I while the bands at 14.7–17.3 kK are assigned to transition II. It is possible, of course, that these assignments should be reversed, as has been proposed for other cases,[3,14] and it is unfortunate that the poor resolution of the bands does not permit more detailed study. Transition III may be barely discernible as a shoulder at *ca.* 21 kK in the reflectance spectrum of $VO(ebas)_2$.

Spectra measured in the coordinating solvents dimethyl sulfoxide and pyridine (Figure 3) show a band at about 16 kK that corresponds well with the band assigned above to transition II. The resolution of the band was satisfactory in all solvents studied only in the case of $VO(ebas)_2$, and in this case a red shift was observed in the coordinating solvents. The shoulders found at 10.5–12.1 kK in 1,2-dibromoethane are shifted to the blue in coordinating solvents. The magnitude of the shift is very difficult to ascertain owing to the broadness of the shoulders, but it may be as much as 2 kK. The observed red and blue shifts are so poorly defined that conclusions about the spectral assignments are perilous; however, it should be pointed out that similar shifts have been observed by Selbin and coworkers[14] for several β-diketone complexes in which the low-energy shoulder was assigned as transition II. The spectral shifts observed in coordinating solvents do support the view that the complexes can add a sixth ligand.

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Proton Nuclear Magnetic Resonance Investigation of Some Paramagnetic Transition Metal Tris Chelates with Unsymmetrically Methyl-Substituted *o*-Phenanthrolines

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The proton nmr spectra of the Cr(II), Fe(III), Co(II), and Ni(II) tris chelates with a series of unsymmetrically methyl-substituted *o*-phenanthrolines have been observed. A set of four equally intense resonance peaks for a given ligand proton indicates that the two possible geometrical isomers, *cis* and *trans*, are formed in statistical amounts for all complexes. The extent of magnetic dissymmetry for a given metal ion was found to depend on the position(s) of methyl substitution, with the greatest effect noted for methyl groups at the 4 position. Analysis of the isotropic shifts for the Cr(II) and Fe(III) chelates suggests that the π-contact interaction is more sensitive to unsymmetrical methyl substitution than either the σ-contact interaction or the dipolar interaction. For the Co(II) complexes, the magnetic dissymmetry is concluded to arise primarily from the dipolar interaction.

Introduction

A recent analysis[1] of the ligand contact shifts for tris *o*-phenanthroline (phen) and α,α′-bipyridine (bipy) chelates with Cr(II) has indicated that, although metal–ligand π bonding is present, it plays a relatively minor role in the spin-delocalization mechanism, in spite of the fact that these ligands had been previously considered very good π acceptors. It was therefore suggested that the anomalous "spin-only" magnetic moments[2] for these Cr(II) chelates result from a strong trigonal distortion[3] rather than from delocalization[4] of the magnetic electrons.

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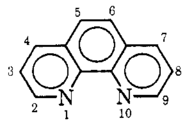
(1) G. N. La Mar and G. R. Van Hecke, *J. Am. Chem. Soc.*, **91**, 3442 (1969).

(2) A. Earnshaw, L. F. Larkworthy, K. C. Patel, K. S. Patel, R. L. Carlin, and E. G. Terezakis, *J. Chem. Soc., A*, 511 (1966).

(3) Y. M. Udachin and M. E. Dyatkina, *J. Struct. Chem.* (USSR), **8**, 325 (1967); *Zh. Strukt. Khim.*, **8**, 368 (1967).

(4) E. G. Terezakis and R. L. Carlin, *Inorg. Chem.*, **6**, 2125 (1967).

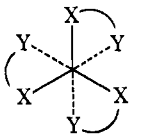
For the Cr(II) complexes, although we were able to demonstrate[1] the presence of some π-spin density[5] at the 3,4,7,8 positions in phen (A), it was not possible to identify which ligand π molecular orbital (MO) contained the unpaired spin. It was suggested[1] that perhaps some indirect spin polarization mechanism is also operative in the π system.



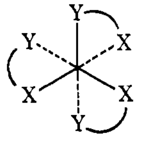
A

In order to determine if our limited understanding of the possible mechanisms of spin delocalization in these complexes can be improved, our proton nmr investigations have been extended to the tris Cr(II) chelates of a series of unsymmetrically methyl-substituted phen ligands. The analogous chelates with the metal ions Fe(III),[6-8] Co(II),[9] and Ni(II)[9] are included for comparison.

For tris chelates of unsymmetrical bidentate ligands, designated XY, two geometrical isomers may be formed, the *cis* (B) and the *trans* (C) forms. In the former isomer, all three ligands are equivalent, and it possesses C_3 symmetry; in the *trans* isomer, the three ligands are nonequivalent, the symmetry being only C_1. In a statistical mixture of these two isomers in solution, four equally intense peaks per ligand position are expected.[10] In diamagnetic complexes, the magnetic nonequivalence of the ligand protons in the two isomers or within the *trans* isomer is often below the resolving power of the spectrometer or is obscured by natural line widths (~1 Hz), making detection of the isomers impossible by nmr. However, it has been recently shown that due to the nonlinear expansion of the proton nmr chemical shift scale in the presence of unpaired electrons in a complex, the two isomers can be readily detected and their relative distribution determined by nmr.[10]



B



C

It is not anticipated that simple unsymmetrical methyl substitution of the ligands would upset the expected statistical mixture of isomers; thus four equally intense peaks per ligand proton should be observed if the proton–electron interaction is sufficiently sensitive to the reduced molecular symmetry. However, the ability to introduce ligand asymmetry by such as small perturbation as a single methyl group, coupled with the ability to vary the position(s) of the methyl substituent(s), presents a unique opportunity to test the sensitivity of the nmr technique for detecting the geometrical isomers and to determine for which ligand position the methyl substitution produces the largest magnetic dissymmetry.

Last, since the shifts for these various complexes involve both contact interactions with delocalized σ as well as π electrons and dipolar shifts due to magnetic anisotropy,[5] it is of interest to determine which of these three distinct types of proton–electron coupling mechanisms are most affected by the reduction in molecular symmetry due to unsymmetrical methyl substitution.

Experimental Section

Complexes.—All reactions and handling of the Cr(II) chelates were performed under an N_2 atmosphere using degassed solvents. The Cr(II) and Fe(III) complexes were prepared in the same way as were the chelates with symmetric ligands.[1,2] The metal salts were obtained from Alfa Inorganics, Inc., and the ligands from G. F. Smith Chemical Co. The tris complexes of $CoCl_2$ and $NiCl_2$ were prepared in a similar fashion. The parent complexes of symmetric ligands have all been well characterized, and for Fe(III) all unsymmetrically substituted complexes have also been reported.[8] Analyses for the new Cr(II) complexes and some of the Co(II) and Ni(II) complexes are given in Table I.

TABLE I

CARBON AND HYDROGEN ANALYSES

	Anal, %			
	Calcd		Found	
Complex	C	H	C	H
$(4\text{-phen})_3CrCl_2 \cdot H_2O$	64.6	4.4	64.5	4.5
$(4\text{-phen})_3CoCl_2 \cdot 2H_2O$	63.6	4.7	63.1	5.0
$(4\text{-phen})_3NiCl_2 \cdot 2H_2O$	63.6	4.7	62.6	4.7
$(5\text{-phen})_3CrCl_2 \cdot H_2O$	64.6	4.4	65.8	4.5
$(3,4\text{-phen})_3CrCl_2 \cdot H_2O$	65.6	5.5	66.0	5.1
$(3,4\text{-phen})_3CoCl_2 \cdot 2H_2O$	63.9	6.0	62.2	4.6
$(4,5\text{-phen})_3CrCl_2 \cdot H_2O$	65.6	5.5	64.1	5.1
$(4,6\text{-phen})_3CrCl_2 \cdot H_2O$	65.6	5.5	65.4	5.0
$(4,6\text{-phen})_3CoCl_2 \cdot H_2O$	65.1	5.5	65.5	5.2

The nmr samples were prepared by dissolving the Cr(II) in methanol-d_4 (Diaprep, Inc.) and sealing under N_2. The Fe(III) samples were prepared by bubbling chlorine gas through a D_2O (Bio-Rad Laboratories, Inc.) solution of the ferrous chelate in the absence of light.[6,11] The Co(II) and Ni(II) samples were dissolved in methanol-d_4 under N_2, and the tubes were simply capped.

For the sake of brevity, *o*-phenanthroline will be referred to as phen, and the position(s) of methyl substitution will be simply designated by number as in A. Thus, 3,4-dimethyl-*o*-phenanthroline is represented by 3,4-phen.

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(5) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

(6) D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **41**, 908 (1964).

(7) R. E. DeSimone and R. S. Drago, *J. Am. Chem. Soc.*, **92**, 2343 (1970).

(8) The Fe(III) chelates are part of a well-characterized series of complexes: W. W. Brant and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949).

(9) M. Wicholas and R. S. Drago, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968, No. INOR 123.

(10) (a) F. Rörscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967); (b) *ibid.*, **6**, 1607 (1967); (c) *J. Am. Chem. Soc.*, **89**, 6472 (1967).

(11) Although the Fe(III) chelates produced by this technique[6] are relatively unstable at 30°, their nmr spectra remain invariant over several hours at 0°. Even when decomposition is noted by a slight color change to red, the Fe(III) complex peak positions remain fixed, though their line widths increase and intensities decrease. Also, the paramagnetic shifts for all peaks are proportional to the amount of Cl_2 present until complete oxidation is effected, indicating that only one species is present. Thus the previous nmr data[1,6] must be characteristic of these chelates in D_2O. Furthermore, the present observation of the four peaks per ligand position for the isomer mixture resulting from asymmetric ligand substitution confirms that we have tris chelates which are nonlabile on the nmr time scale. On the other hand, the possibility of a weak equilibrium involving ligand protonation or ligand acid attack in strongly acidic solution (D_2SO_4 used in ref 7) has not yet been satisfactorily ruled out.

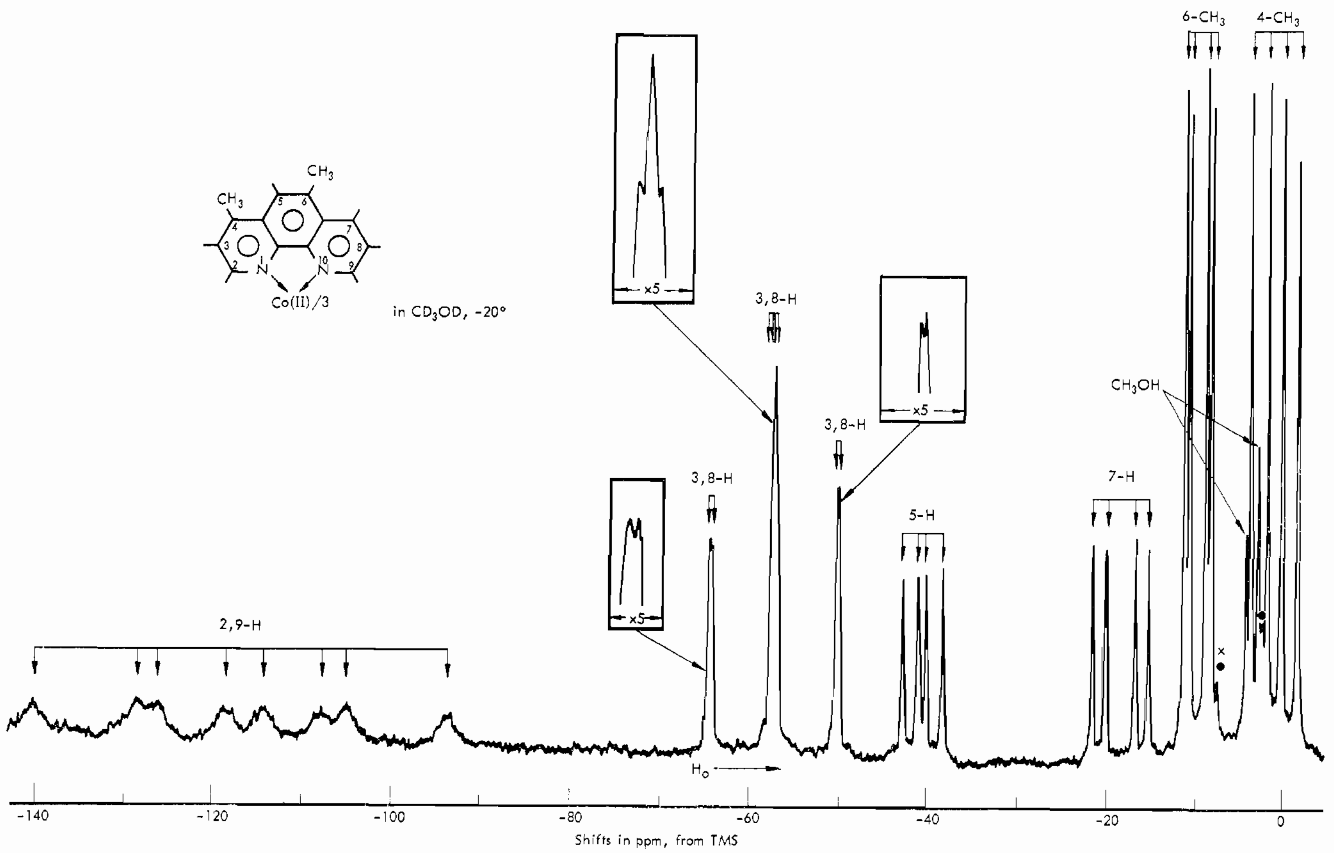

Figure 1.—Proton nmr trace of (4,6-phen)$_3$CoCl$_2$ in methanol.

Nmr Spectra.—The proton nmr spectra were recorded on a Varian HR-100 spectrometer, modified to operate with variable-modulating frequency and employing conventional audio-side-band techniques for calibration. Unless otherwise specified, the solution temperature was maintained at 33°. The internal calibrants were TMS for the methanol solutions and sodium 3-(trimethylsilyl)-1-(propanesulfonate) for the D$_2$O solutions. The proton spectra for all 4-CH$_3$-substituted Cr(II) chelates were recorded at $\sim$5° intervals between -40 and $+50$°.

The isotropic shifts are referenced against the diamagnetic ligand. Inasmuch as only very qualitative use will be made of the observed shifts, the small differences between the ligand shifts and the diamagnetic Fe(II) chelates (less than 60 Hz for any position) are insignificant. All shifts are reported in ppm, and line widths are cited in hertz at 100 MHz. The isotropic shifts for proton peaks which are not directly observable at 33° due to overlap with other peaks are obtained by extrapolating the straight line of the observed shifts *vs.* temperature at higher or lower temperatures to 33°.

Results and Discussion

The reduction of the ligand symmetry upon unsymmetrical methyl substitution can (for any given ligand) at most cause a doubling of any of the four peaks arising from the symmetrically equivalent ring positions. Thus the fact that considerably more than just eight peaks are observed for most complexes indicates that the ligands in the two isomers have significantly different isotropic shifts.

Assignment of Peaks.—The difficulty in obtaining unambiguous assignments depends greatly on the metal ion involved. The assignments for the Co(II) chelates are trivial, since the unsymmetrical substitution results in only a small splitting of the widely separated peaks observed in the complex of the analogous symmetric ligand. The simplicity of the Co(II) nmr spectra is illustrated in Figure 1 for (4,6-phen)$_3$CoCl$_2$ for which 31 of the theoretical 32 peaks are resolved. The complete listing of all complexes is given in Table II. It is not possible to differentiate among the eight lines arising from the paired positions 2,9-H, 3,8-H, 4,7-H, or 5,6-H unless one of the two is methyl substituted.

Assignments for the Fe(III) chelates are reached in a manner similar to that used for the Co(II) compounds, since the methyl substitution in general produced splittings of the peak for the symmetric ligand which are small compared to the average isotropic shift, thereby allowing assignment by analogy to the complexes of symmetric ligands. Only the sets of peaks arising from 3,8-H and 5,6-H overlapped, but here a ready distinction could be made since the 3,8-H lines are $\sim$1.5 times broader[1] than the 5,6-H lines. For the 3-phen and 5-phen complexes, low solubility prevented an accurate determination of the relative peak areas and line widths. The consistency of the shifts for these two complexes with the other complexes, however, supports their assignments. A complete listing of shifts appears in Table III.

The Cr(II) nmr spectra are considerably more complex, since interference or overlap occurs for almost all sets of resonances except the 2,9-H peaks. Thus the resonance spread of the four peaks arising from a given ligand position is often much greater than the isotropic shift for the proton in the complex with the analogous symmetric ligand, particularly for the

TABLE II

ISOTROPIC SHIFTS FOR $(X\text{-phen})_3CoCl_2$[a]

	phen[b]	3-phen	4-phen	5-phen	3,4-phen	4,5-phen	4,6-phen
			−109.30				−111.3
			−103.50		−102.7		−103.5
		−99.50	−101.90	−96.60	−97.70	−94.80 (2)	−100.4
		−97.60	−98.10	−95.40 (3)[c]	−96.00 (3)	−93.60 (2)	−97.20
2,9	−96.50	−95.00 (2)	−96.10	−92.70 (3)	−93.80	−91.30 (2)	−93.70
		−93.50 (4)	−92.60	−90.30	−89.70	−89.90 (2)	−89.65
			−90.75		−88.60		−87.60
			−85.05				−79.90
		[−0.48][d]			[−2.52]	−37.17	−36.75 (2)
3		[−0.61]			[−2.06]	−37.52	−40.42
		[−0.95]	−36.60 (2)		[−0.77]	−39.23	−41.48
	−39.95	[−1.17]	−40.80 (2)	−41.25 (4)	[−0.61]	−39.57	−41.65
		−42.05	−41.17 (2)	−42.20 (4)	−37.35	−42.02	−41.75
8		−41.75	−45.30 (2)		−37.65	−42.35	−46.28
		−41.20 (2)			−40.45 (2)	−44.05	−46.50
						−44.40	
		−7.21	[+3.17]		[+2.84]	[+3.56]	[+3.33]
4		−7.32	[+2.14]	−8.10	[+2.00]	[+2.99]	[+1.87]
		−7.48	[+1.33]	−8.21	[+1.50]	[+2.67]	[+0.85]
	−7.28	−7.89	[+0.17]	−8.64 (4)	[+0.77]	[+2.09]	[−0.67]
	[+3.38]	−8.41 (2)	−5.87	−9.15	−6.12	−7.25	−5.62
7		−8.66	−6.87	−9.24	−7.40	−8.06	−6.18
		−8.95	−8.67		−8.60	−8.94	−8.39
			−9.74		−9.63	−9.73	−9.56
			−22.90		−23.45	[−7.00]	−23.78
5			−23.95	[−5.56] (2)	−24.68	[−6.56]	−25.05
	−23.03		−24.65	[−5.76] (2)	−24.95	[−6.13]	−25.65
		−24.02 (4)	−25.10		−25.28	[−5.68]	−26.80
		−24.86 (4)	−25.68	−23.60	−26.22	−21.42	[−4.20]
6			−26.18	−23.45 (2)	−26.38	−22.24	[−4.62]
			−26.75	−23.30	−26.70	−22.85	[−5.80]
			−27.83		−27.85	−23.62	[−6.29]

[a] Shifts in ppm, at 33°, in CD_3OD solution, referenced against diamagnetic ligand. [b] The shifts for the unsubstituted complex are included for comparison. The methyl shifts at any position in a symmetric ligand are given in brackets.[9] [c] The number of overlapping peaks is given in parentheses. [d] The methyl shifts are given in brackets.

TABLE III

CONTACT SHIFTS FOR $(X\text{-phen})_3FeCl_3$[a]

	phen[b]	3-phen	4-phen	5-phen	3,4-phen	4,5-phen	4,6-phen
			+59.95 (2)		+60.20 (2)	+57.60 (2)	+59.15 (2)
2,9	+56.02	+55.90 (8)[c]	+55.04 (4)	+58.35 (8)	+55.35 (4)	+54.80 (4)	+54.75 (4)
			+49.20 (2)		+49.50 (2)	+51.70 (2)	+48.55 (2)
			+13.07		[+2.50][d]	+12.41	+13.28
3		[+2.11] (2)	+12.31		[+1.85] (2)	+11.99	+12.46
	+10.52	[+2.17] (2)	+11.86		[+1.13]	+11.32 (2)	+12.20
	[+1.83]		+11.15	+10.85 (4)		+10.08	+11.15
			+9.63	+10.60 (4)	+14.03	+9.59	+9.50
8		+10.15 (2)	+8.94		+13.00	+8.89	+8.70
		+7.48 (2)	+8.30		+10.55	+7.61	+7.93
			+7.38		+9.00		+6.88
			[−14.48]		[−15.57]	[−14.62]	[−14.86]
4			[−15.77]		[−16.78]	[−15.48]	[−16.22]
	−0.46		[−18.44]		[−20.53]	[−17.63]	[−19.20]
		+2.50 (8)	[−20.10]	+2.09 (8)	[−22.13]	[−18.79]	[−21.03]
	[−13.49]					+1.66	+3.32
7			+2.64 (4)		+2.22 (4)	+2.15	+2.57
						?	+2.45
						?	+1.78
			+6.93		+6.84		+6.39
5			+6.08	[+1.93] (2)	+6.18	[−2.85] (4)	+5.53
	+6.53	+6.68 (2)	+5.89	[+0.91]	+4.46		+3.95
	[+1.40]	+6.37 (2)	+3.81		+3.91		+3.20
		+3.75 (2)	+1.72 (2)		+3.56 (2)	+6.67	
6		+3.25 (2)	+1.50	+5.08 (4)	+2.22	+6.31	[−1.08] (?)
			+1.18		+1.29	+4.96	
						+4.40	

[a] See footnote *a* in Table II, except that D_2O solutions were used. [b] See footnote *b* in Table II. [c] See footnote *c* in Table II. [d] See footnote *d* in Table II.

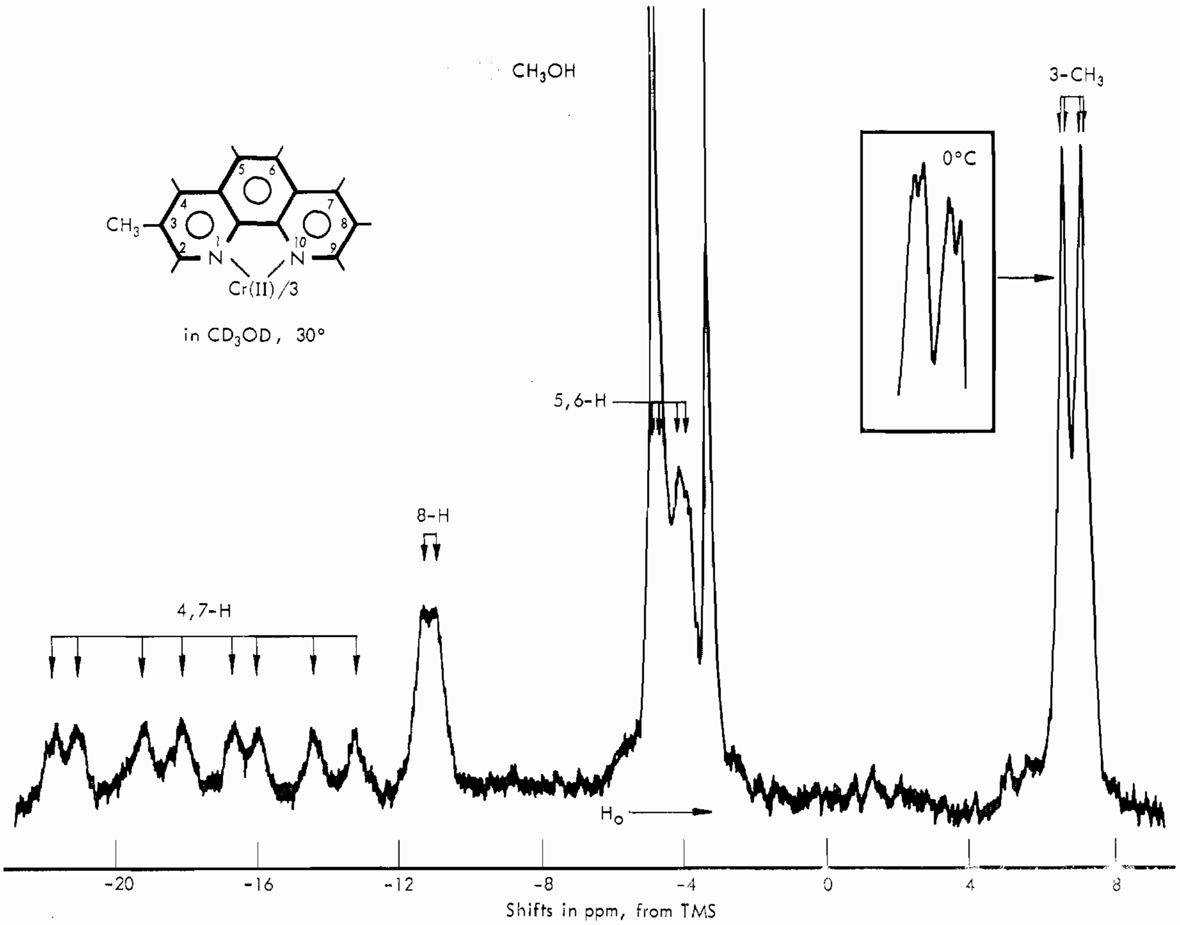

Figure 2.—Proton nmr trace of (3-phen)$_3$CrCl$_2$ in methanol at 30° (2,9-H peak not shown).

4-CH$_3$-substituted chelates. However, unambiguous and self-consistent assignments for all peaks is feasible with the aid of relative line widths, areas, and the temperature dependence of the isotropic shifts.

For the 3-phen and 5-phen chelates, only very small splittings are observed, so that assignments are readily made by comparison with the phen chelate. The expected four resonances per ligand proton are realized only for 4,7-H and for 3-CH$_3$ in 3-phen at low temperature as shown in Figure 2. For the remaining complexes, the most serious overlap occurs between methyl and aromatic protons, as illustrated in Figures 3 and 4. However, since the methyl and aromatic protons have diamagnetic resonances differing by ~5 ppm, the two types of protons will have significantly different temperature dependences. Thus recording the proton spectra at ~5° intervals between −30 and 45° allows one to observe, for example, each of the eight 5,6-H and eight 3,8-H peaks unobscured over some range of temperature. Four such proton traces are reproduced in Figure 3, which locates each of the expected 24 3,4,5,6,7,8-H peaks at at least one temperature. In fact, two 3,8-H resonances, c and d in Figure 3, are accidentally degenerate at all temperatures, so that, although all 24 peaks are accounted for, only 23 separate resonances are observed. The methyl peaks are easily located by their intensities. The two sets of eight equally intense and equally broad peaks assigned to the 3,8-H and 5,6-H can again be differentiated because the 3,8-H lines are 50% wider than the 5,6-H peaks.[1] The four farthest downfield aromatic peaks must arise from the 7-H on the basis that only four peaks appear in that set, as expected, and that the 4,7-H resonates farthest downfield in both 3-phen and 5-phen and in all symmetric ligand complexes. The assignment is confirmed by effect of an additional methyl substituent at either the 3, 5, or 6 positions, as shown in Table IV.

Comparison of the data in Table IV for the 4-CH$_3$-substituted complexes demonstrates that the spread of the four peaks per ligand proton is more or less insensitive to the position of or even the presence of the second substituent. Comparison of the 4-phen and 3,4-phen complexes, shown in Figures 3 and 4, illustrates that the addition of the 3-CH$_3$ in Figure 4 has primarily the effect of eliminating the 3,8-H peaks e–h, in Figure 3; the remaining resonance positions are essentially unaffected. This not only serves to confirm the assignment of the set of eight peaks to 3,8-H in the 4-phen complex but allows a distinction to be made between the 3-H and 8-H peaks in the 4-phen complex, with a–d belonging to 8-H and e–h to 3-H. This distinction is again confirmed in the 4,5-phen and 4,6-phen complexes. Similar comparisons between the 4-phen complex and each of the 4,5-phen and 4,6-phen chelates serves to distinguish between the 5-H and 6-H peaks in all 4-CH$_3$-substituted complexes.

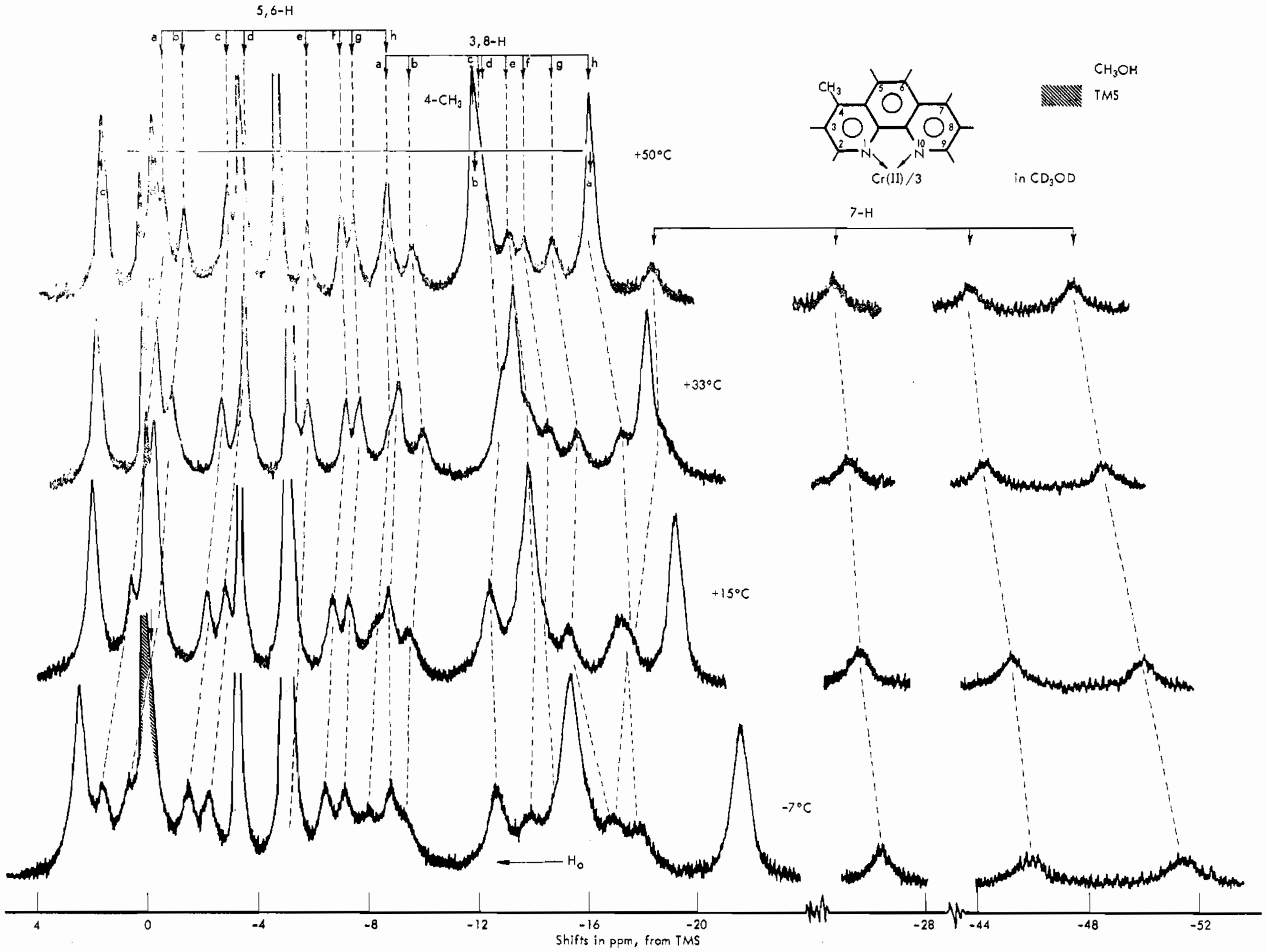

Figure 3.—Proton nmr traces of (4-phen)$_3$CrCl$_2$ in methanol at −7, +15, +33, and +50° (2,9-H peaks not shown).

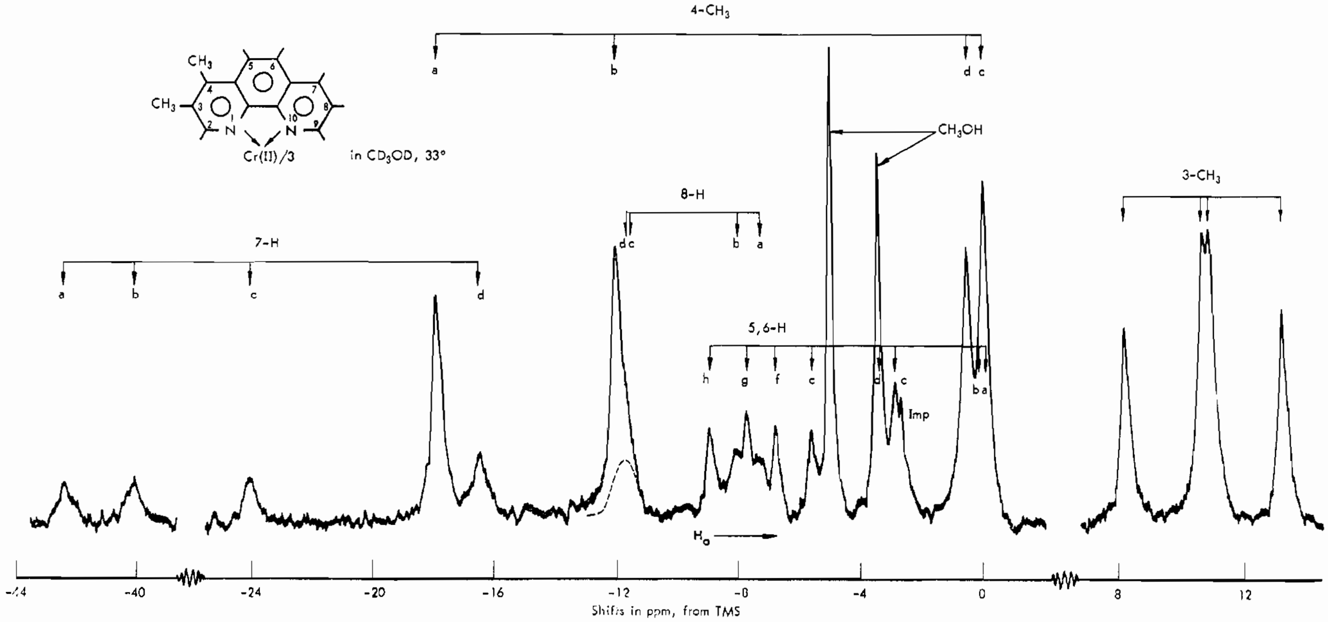

Figure 4.—Proton nmr trace of (3,4-phen)$_3$CrCl$_2$ in methanol at 33° (2,9-H peaks not shown).

The fact that the 7-H resonances in the 4-CH$_3$-substituted ligands are slightly broader than the 3,8-H and increase in width as the isotropic shift increases arises from the fact, for all peaks except 7-H, the contact shifts are sufficiently small so as to guarantee that the dipolar relaxation mechanism is dominant, leading to an approximately r^{-6} dependence of the line width, where r is the proton–metal distance. How-

TABLE IV

CONTACT SHIFTS FOR (X-phen)$_3$CrCl$_3$[a]

	phen[b]	3-phen	4-phen	5-phen	3,4-phen	4,5-phen	4,6-phen
2,9			+44.02 (2)		+41.70 (?)	+42.10 (?)	+47.60 (?)
	+30.00	+28.05 (8)[c]	+31.55 (4)	+30.56 (8)	+30.30 (?)	+32.10 (?)	+33.40 (?)
			+27.00 (2)				
3			−8.07		[+16.21][d]	−9.14	−9.27
		[+9.69] (2)	−7.64		[+13.89]	−7.50	−7.10
	−4.77	[+9.25] (2)	−6.62		[+13.14]	−6.43	−6.30
			−5.90	−5.23 (4)	[+11.31]	−5.43	−5.72
8	[+10.02]		−4.08 (2)	−5.56 (4)	−4.00 (2)	−5.38	−4.10 (2)
		−3.68 (2)	−1.54		−0.10	−4.87	−1.95
		−3.47 (2)	−0.58		+0.60	−2.66	−0.69
						−1.62	
4		−5.47	[+4.19]	−6.78	[+2.70]	?	[+2.92]
		−6.28	[+2.27]	−7.44	[+2.17]	[+0.60]	[+0.70]
	−10.53	−7.68	[−9.38]	−8.61	[−9.05]	[−12.43]	[−12.23]
	[+6.83]	−8.08	[−13.74]	−9.27	[−14.64]	[−16.30]	[−17.45]
7		−10.06	−8.70	−10.87	−6.93	−7.34	−8.47
		−10.83	−15.56	−11.50	−15.65	−14.74	−16.97
		−12.63	−29.95	−12.72	−32.50	−29.67	−33.15
		−12.89	−33.90	−13.42	−35.10	−33.52	−38.40
5			+7.80		+8.10	[−3.36]	+7.10
			+7.05	[+0.36] (2)	+7.80	[−2.96]	+6.55
	+3.57	+3.99 (2)	+5.43	[+0.21] (2)	+5.30	?	+5.62
	[+0.35]	+3.79 (2)	+4.47		+4.75	?	+4.75
6		+3.52 (2)	+2.62		+2.64	+2.35	[+3.19]
		+3.33 (2)	+1.38	+3.71 (4)	+1.52	+1.56	[+2.32]
			+0.93		+0.62	+0.39	[+1.77]
			−0.32		−0.57	−0.74	[+0.55]

[a] Shifts in ppm, at 33°, in CD$_3$OD solution, referenced against diamagnetic ligand. [b] See footnote *b* in Table II. [c] See footnote *c* in Table II. [d] See footnote *d* in Table II.

ever, for contact shifts greater than ~15 ppm, the hyperfine exchange relaxation mechanism becomes important for 4,7-H and makes significant contributions to the line width,[12] leading to a line width proportional to the square of the shift.[13]

Stereochemistry and Magnetic Dissymmetry.—The fact that for each complex studied, with the exception of (3-phen)$_3$FeCl$_3$ and (5-phen)$_3$FeCl$_3$, four equally intense peaks are observed for at least one ligand proton demonstrates that both the *cis* and *trans* isomers are present in the statistical ratio of 1:3. Neither the metal ion nor the position(s) of methyl substitution affect(s) the isomer distribution. For the 3-phen and 5-phen chelates of Fe^{3+}, it is only possible to state that both isomers must be present, since the 8-H in the former and the 5-CH$_3$ in the latter complex each display two equally intense lines. The *cis* isomer alone can result in only one line for each position, while for the *trans* isomer, when only *two* peaks are observed, the intensity ratio must be 2:1. These two sets of two peaks are consistent with the statistical isomer ratio if one of the *trans* peaks and the *cis* peak, and the two remaining *trans* peaks, are each accidentally degenerate.

The proton nmr traces of the spin-paired Fe(II) chelates[8] are similar to those for the free ligand, with no indications of peak splittings, so that no evidence for the isomer distribution can be obtained in a diamagnetic complex. The fact that the two isomerscan be so readily detected in a paramagnetic complex, in spite of the minute perturbation of ligand or complex structure anticipated from simple methyl substitution, serves to illustrate the extreme sensitivity of this nmr technique.

The facility to detect unambiguously the presence of the two geometrical isomers in solution by nmr depends on the position of substitution. For monosubstituted ligands, the extent of magnetic dissymmetry, as measured by the relative spread[14] of the four resonances from a ligand proton, varies as 4-phen ≫ 3-phen ~ 5-phen, for all the metal ions. The ordering of the effects of substituent position on magnetic dissymmetry is similar to the relative perturbations on the ligand basicity[15] or on the half-wave potential for the Fe^{2+}-Fe^{3+} couple[8] for the tris chelate of that ligand, where the 4-CH$_3$ affects the average nitrogen lone-pair electron energies more than the 3-CH$_3$ or 5-CH$_3$. However, the present nmr results show that the two ligand nitrogens are affected very differently. It is to be remembered that, upon symmetric methyl substitution of the ligands, no significant or systematic effect of substitution position on spin delocalization or bonding could be gleaned from the nmr contact shifts.[1,6] A major difference therefore exists between our nmr data and the

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(12) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961).

(13) The proton line width contributions from the dipolar and contact relaxation mechanisms, in the limit of fast motion, are $1/T_2 = [S(S+1)\cdot\gamma_I^2 g^2\beta^2/15r^6]_D\tau + [S(S+1)A^2/3\hbar^2]_C\tau$. For 4,7-H, $r^{-6} = \sim 2.5 \times 10^{-48}$ cm^{-6}, such that $[\,]_D \simeq 9 \times 10^{11}$. For a contact shift of ≃15 ppm, $[\,]_C \sim 9 \times 10^{11}$. Thus for contact shifts greater than 15 ppm, the contact exchange mechanism is dominant, while for contact shifts less than 15 ppm, the dipolar term is dominant.

(14) The spread of the four peaks from a ligand position should only be compared in different complexes when the two protons which were equivalent in the symmetric ligand can be differentiated; otherwise the spread of the *eight* resonances will include effects arising purely out of ligand asymmetry as well as the magnetic dissymmetry which results upon complex formation.

(15) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths and Co. Ltd., London, 1965.

data on ligand basicities and Fe(II)–Fe(III) half-wave potentials.[16] The latter data have shown that multiple substitution produces additive effects;[15,16] the nmr data demonstrate conclusively that this is *not* the case if comparison is made between chelates with symmetric and asymmetric ligands.

From the data available, it is not possible to specify which one of the four resonances for a ligand position belongs to the *cis* isomer. However, for the 4-CH_3-substituted Cr(II) chelates, where the four 4-CH_3 and 7-H peaks experience widely differing chemical shifts, it is apparent in Table IV that one 4-CH_3 (~3–4 ppm) and one 7-H peak (~−15 ppm) appear approximately at the same position as in the complex of the related symmetric ligand, while the remaining three resonances are shifted, some considerably. Since both the *cis* isomer and the complexes with symmetric ligands have trigonal symmetry, the close resemblance between the two unshifted 4-CH_3 and 7-H peaks suggests they belong to the *cis* isomer. This tentative assignment is strongly supported[17] by the detailed analysis of the anomalous temperature dependence of the contact shifts in these Cr(II) chelates.

Origin of Isotropic Shifts.—The origin of the observed isotropic shifts for the complexes of the three metal ions is analyzed primarily for the purpose of comparison with the chelates of the analogous symmetric ligands. In particular, it would be useful to know which of the three possible contributions to the isotropic shifts—σ contact shifts, π contact shifts, or dipolar shifts—are the most sensitive to the reduction in molecular symmetry. The relative spread in resonance position of the four peaks[14] belonging to a given proton can be considered a reasonable index of the sensitivity of the particular interaction which dominates that isotropic shift.

Cr(II) Complexes.—Analysis of the complexes with symmetric ligands[1] has shown that at least the 3,4,7,8 positions are dominated by π-spin density and that dipolar shifts[18] are essentially negligible at these positions. These conclusions[1] were based on the observation that the proton and methyl shifts at a position were of comparable magnitude but of opposite sign, as predicted for π-spin density, and that these shifts were in strong disagreement with dipolar shifts, which predict[1] proton and methyl shifts with the same direction, with the latter much smaller than the former. The 2,9-H, 5,6-H, and 5,6-CH_3 shifts were shown[1] to be inconsistent with either π-spin density or only dipolar shifts. This inability to account for the anomalous upfield shifts at the 2,9 and 5,6 positions by the dipolar interaction led us to postulate the delocalization of negative (β) σ-spin density[19] (*vide infra*).

Inspection of Figures 2 and 3 and the data in Table IV demonstrates that the largest change in shifts upon methyl substitution occur for the 4,7 protons and methyl groups. Inasmuch as the geometric factors, which determine the relative dipolar shifts, decrease[1] in the order 2,9-H > 3,8-H ~ 5,6-H > 4,7-H, while the observed trend in the magnitude of the splittings is 4,7-H > 2,9-H ~ 3,8-H ~ 5.6-H, it can be concluded that the π-contact interaction is more sensitive to the reduced ligand symmetry than either the delocalized σ-spin density or the dipolar interaction.

It has been shown that in the *trans* isomer of the tris chelates of other unsymmetrical bidentate ligands,[10] the π-contact shifts for the three nonequivalent ligands display slightly different patterns. Thus there is not only a simple difference in the amount of spin delocalization into the three ligands, but the spin delocalization conforms to the full molecular symmetry (or lack of it) in the *trans* isomer.[10]

For the present complexes, a simple 4-CH_3 substitution, which is not expected to perturb the ligand MO's significantly, results in sizable variation in magnitudes for both 4-CH_3 and 7-H shifts and a change of sign for the 4-CH_3 shifts; two of the four 4-CH_3 shifts are negative, in contrast to complexes with symmetric methyl substituents.[17,20] Thus for the *trans* isomer, two ligands have spin density of different sign at C_4 than the third ligand. It is considered highly improbable that the metal spins interact with totally different ligand π MO's in each ligand, so that the possibility of an indirect π-delocalization mechanism in addition to direct delocalization may have to be considered.

The sizable increase in the magnitudes of some of the 4-CH_3 and 7-H shifts in the chelates with asymmetric ligands does bring up the possibility that the surprisingly small π-contact shifts observed[1] for the chelates with symmetric ligands do not necessarily reflect lack of extensive π delocalization[1] and rather may result from a fortuitous near cancellation of spin densities of opposite signs in different orbitals. Thus the reduction in ligand symmetry may cause an imbalance of the competing mechanism and, hence, considerably larger π-contact shifts. This possibility is being currently investigated.

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(16) P. Day and N. Sanders, *J. Chem. Soc., A*, 1530 (1967).

(17) G. N. La Mar and G. R. Van Hecke, *J. Am. Chem. Soc.*, **92**, 3021 (1970). (For these Cr(II) chelates, the relative magnitudes of the observed 4-CH_3 and 7-H shifts result in part not from different extents of covalency for the three ligands in the *trans* isomer but from a difference in the availability of unpaired spin in the proper metal d orbital. However, the different *signs* of the three *trans*-isomer 4-CH_3 shifts must arise from different π-delocalization mechanisms.)

(18) Attempts to directly determine the magnetic anisotropy for $(phen)_3CrCl_2$ failed. A dilute methanol glass at 77° produced no observable esr signal between ~800 G ($g \approx 0.5$) and ~5800 G ($g \approx 3.5$), using a Varian X-band esr spectrometer.

(19) This mechanism has been discussed by L. E. Orgel, *Discussions Faraday Soc.*, **26**, 92 (1958); *J. Chem. Phys.*, **30**, 1617 (1959), who specifically postulated that for the σ lone-pair ligand electrons donated to a metal ion with no electrons in σ-bonding (e_g) d orbitals, but unpaired spins in the t_{2g} set, there will be a distinct energetic preference for the donation of positive (α) spin over negative (β) spin, due to the more favorable exchange interaction with the t_{2g} spins. Since the ligand lone-pair electrons must be paired over the MO, the preference of donating positive spin to the metal results in a net *negative* σ-spin density in the ligand. Although the extent of unpairing of the lone-pair electrons by the t_{2g} spins may be considerably smaller than for a similar unpairing of a filled d orbital by some unpaired d electrons, due to the larger energy difference in the former interaction, the fact that the net negative σ-spin density ends up in an MO which is primarily *ligand* in character should allow it to be detected by nmr.

(20) A Hückel spin-density calculation of 4-phen, using a methyl inductive parameter of $\alpha_{C_4} = \alpha + 0.5\beta$, leads to only a ~25% difference in spin density between C_4 and C_7. In addition, a similar difference is predicted for both 3-phen and 5-phen, contrary to the significant difference in magnetic dissymmetry between 4-phen and 5-phen or 3-phen.

This inability to characterize the spin-containing π MO on the basis of π-contact shifts at two ligand positions indicates the danger in overemphasizing the assignment of the mode of spin delocalization into ligands where only one position experiences primarily π-spin density.

Fe(III) Complexes.—In a previous report[1] we postulated that the dominant spin-delocalization mechanism in the tris chelates with symmetric ligands involved negative σ-spin density due to exchange polarization between the nitrogen lone pair and the metal unpaired t_{2g} electrons[19] and that direct π delocalization was only modest and apparent only at the 4,7 position. A recent esr analysis[7] of some of these Fe(III) chelates has demonstrated that the g tensors are highly anisotropic, with resultant large dipolar shifts for some ligand protons. These esr results[7] lead the authors to claim that our qualitative analysis of the observed shifts in terms of negative σ-spin delocalization was therefore totally invalid because we failed properly to assess magnetic anisotropy. We do not question the validity of the esr data nor the claim that our ignoring dipolar shifts in the Fe(III) chelates was not warranted. However, our conclusions as to the dominant delocalization mechanism we reached *in spite* of possible dipolar shifts are not negated by the esr data, so that we dispute only the applicability of the esr data in disproving negative σ-spin delocalization.

First, we did consider the possible consequences of dipolar shift on our interpretation;[1] it was explicitly stated that a test calculation based on the maximum possible anisotropy would yield a 2,9-H dipolar shift of only +27 ppm (which is *less* that the experimentally observed value), which could account for only half of the sizable upfield 2,9-H shift, and the remaining +27 ppm 2,9-H *contact* contribution would still be inconsistent with π delocalization, since this position will have the smallest π-spin density in orbitals likely to interact with the metal. Hence, we postulated[1] negative σ-spin density to be present.

Second, the authors did not include[7] the extensive nmr data on the methyl-substituted phenanthroline chelates,[11] whose analysis in terms of the reported g values, given in Table V, not only serves to disprove their claim that the *contact* contributions to the observed shifts are completely consistent with π-spin density but also can be considered support for the postulated negative σ-spin density mechanism. Therefore, as the data in Table V illustrate, even after subtracting the calculated dipolar contributions, the proton contact shifts are all upfield (though MO calculations predict both positive and negative spin density[1]), and, although there is indeed a sign reversal between proton and methyl shifts at the 3,8 and 4,7 positions (suggesting π-spin density, as also observed for Cr(II) chelates[1]), the shifts for the 5,6-H and 5,6-CH_3 are *both upfield.* This inconsistency for the 5,6 shifts is outside the error introduced by the assumed geometric factor and does not depend on the exact magnitude of the dipolar shift, such that using the g values for the phen chelate[7] is valid. This inconsistency of the 5,6- and 2,9-H shifts with *any combination of only π-spin density and dipolar shifts* was specifically noted[1] for both Cr(II) and Fe(III) chelates. Thus a mechanism other than π-spin density and a dipolar interaction must be operative. Since the anomalous interaction produced *upfield* shifts and low-spin Cr(II) or Fe(III) possesses no unpaired σ-bonding electrons, the indirect polarization mechanism seems the most plausible. The resulting *contact* shifts from Table V (based on the Larsen–Wahl data[6]) follow the order 2,9-H > 3,8-H < 5,6-H, which, although inconsistent with π-spin density,[1] are qualitatively in line with the expectations for σ delocalization, in that the order is 2,9-H > 3,8-H, 5,6-H. If the $(phen)_3Fe^{3+}$ data of DeSimone and Drago are used, the ordering of shifts is identical with that of the Ni(II) chelates, 2,9-H > 3,8-H > 5,6-H. Quantitative agreement between the relative Ni(II) shifts and the contact shifts of the Fe(III) chelates cannot be expected since some π delocalization is present in both systems.

TABLE V

SEPARATION OF DIPOLAR AND CONTACT SHIFTS FOR SUBSTITUTED $(phen)_3Fe^{3+}$ COMPLEXES[a]

Position	Obsd shift[b]	Rel geometric factors[c]	Calcd dipolar shift[d]	Contact shift
2,9-H	+55.0	+1.000	+25.4	+29.6
3,8-H	+10.8	+0.14	+3.6	+7.2
4,7-H	−0.6	−0.068	−1.7	+1.1
5,6-H	+5.0	−0.16	−4.1	+9.1
3,8-CH_3	+1.8	+0.11	+2.8	−1.0
4,7-CH_3	−14.0	−0.044	−1.1	−12.9
5,6-CH_3	+1.0	−0.10	−2.5	+3.5

[a] All shifts in ppm, at 23°, taken from ref 6. [b] Shifts are typical for each position, having been observed in at least two different complexes. [c] Relative geometric factors are taken from ref 1 and differ insignificantly from those given in ref 7. [d] Calculated dipolar shifts based on esr data in ref 7.

These observations for the Fe(III) and Cr(II) chelates, together with the observations that similar, very large upfield shifts have been reported[21] for V(III) chelates (which contain no e_g electrons), at the precise ligand positions where large downfield σ shifts have been reported for the Ni(II) chelate[21] with the same ligand, lead us to conclude that delocalization of negative σ-spin density[19] cannot be discounted.

Thus, since it has been shown[1,7] that the dipolar shifts at the 4,7 positions are more than an order of magnitude smaller than for 2,9-H, the fact that the observed spread of the 4-CH_3 resonances is comparable to that for 2,9-H (Table III) can be taken as strong evidence that the differences in the four 4-CH_3 shifts arises primarily from differences in the π-contact interaction. In particular, the dipolar interaction is

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(21) The large downfield shifts for a series of Ni(II) chelates, at certain ligand positions, are inconsistent with only π-delocalization and dipolar shifts, and are attributed to direct σ delocalization: R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964); G. W. Everett and R. H. Holm, *ibid.*, **87**, 2117 (1965); R. H. Holm, A. Chakravorty and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966). The same ligand protons in V(III) complexes, with vacant e_g orbitals, but unpaired t_{2g} spins, produce large upfield shifts which are inconsistent with only π-spin density or dipolar shifts: F. Röhrscheid, R. E. Ernst, and R. H. Holm, *ibid.*, **6**, 1607 (1967); *J. Am. Chem. Soc.*, **89**, 6472 (1967).

totally incapable of accounting for the 7–9-ppm spread of the 4-CH_3 peaks, while the four 7-H peaks are not split at all. Thus we conclude that the π-contact interaction is again more sensitive to the reduced molecular symmetry than either the σ-spin delocalization or the dipolar interaction.

Co(II) Complexes.—A detailed analysis of the isotropic shifts for the tris chelates with symmetric ligands has not been reported yet.[9] Before the effects of unsymmetrical ligand substitution can be discussed, a qualitative picture of the origin of the isotropic shifts is required.

For the 4,7 position, the downfield 4,7-H and upfield 4,7-CH_3 shifts must reflect π-spin density, which may or may not be related to any π-spin delocalization. The shifts for the remaining protons are qualitatively consistent with a direct delocalization of σ-spin density, inasmuch as the order of shifts is 2,9-H > 3,8-H > 5,6-H; also, methyl substitution at the 3,8 and 5,6 positions results in shift attenuation without sign reversal.

Distorted octahedral Co(II) complexes are known to possess significant magnetic anisotropy. The presence of sizable dipolar shifts in the $(phen)_3Co^{2+}$ complex can be demonstrated by comparing[22] its isotropic shifts with those of the analogous Ni(II) chelate,[23] which are given in Table VI. For the Ni(II) chelate, the shifts for all but the 4,7 substituents result primarily from direct σ-spin delocalization. Since the σ MO in phen should be relatively unaffected by a change in the metal ion, the same *relative σ contact* shifts should be observed[22] in the Co(II) and Ni(II) complexes for 2,9-H, 3,8-H, and 5,6-H. Comparing these data in Tables II and VI, respectively, reveals that in fact there is a difference in the *relative* shifts, with the former complex experiencing a sizable upfield bias for the 2,9-H shift, a moderate upfield bias for the 3,8-H shift, and a moderate downfield bias for the 5,6-H shift. The relative magnitudes and directions of these differences in observed relative shifts are consistent with the relative geometric factors for the three sets of protons, which have been reported previously.[1] We conclude that the Co(II) complex shows evidence of a sizable dipolar shift similar to that shown to be present for the related complexes with bipyridine.[24] An estimate of ~+60 ppm for the 2,9-H dipolar shift is obtained by factoring[22] the dipolar and contact shifts on the basis of the above assumptions, leading to calculated contact shifts for the Co(II) complex of −157, −48, −3, and −13 ppm for 2,9-H, 3,8-H, 4,7-H, and 5,6-H, respectively. This estimate of the dipolar contribution is very similar to that obtained for the analogous bipyridine chelate of Co(II).[24]

TABLE VI

CONTACT SHIFTS FOR $(X\text{-phen})_3NiCl_2$[a]

	phen[b]	4-phen	3,4-phen
2, 9	−146 ± 15	~−150 ± 15	. . .
3	−41.65	−40.2 (8)[c]	[−6.12] (4)[d]
8			−40.10 (4)
4	−8.95	[+11.22)] (4)	[+12.46] (4)
7	[+11.75]	−9.15 (4)	−8.90 (4)
5	−16.64	−17.10 (4)	−17.10 (8)
6	[−0.95]	−18.30 (4)	

[a] Footnote *a* in Table II. [b] Data taken from ref 9. The methyl shifts in the symmetric ligand are given in brackets. [c] Footnote *c* in Table II. [d] Footnote *d* in Table II.

This factoring procedure[22] for separating the dipolar and contact contributions to observed shifts for Co(II) complexes by comparison with Ni(II) contact shifts, assuming the same *relative* contact shifts in the Co(II) and Ni(II) complexes, has been criticized recently.[25] However, we feel that this technique can have some *qualitative* significance when applied judiciously. In the present case, for example, the separation of dipolar and contact contributions can have qualitative validity if similar ratios of ligand σ-contact shifts are assumed only for the 2,9, 3,8, and 5,6 positions, where σ-spin density is dominant. The assumption of similar shift ratios between any of these ligand positions and the 4,7 shifts, where π-spin density dominates, cannot be justified. The detailed analysis[17] of the temperature dependence of the shifts for these Co(II) chelates serves to confirm the qualitative validity of our factoring procedure *in this particular case*.

Since the isotropic shift patterns for the Co(II) complexes of unsymmetrically substituted ligands closely resemble those of the symmetric ligands, the same interactions must be responsible for their shifts. The resonance spread of a set of four peaks from a ligand proton is rather small compared to the average isotropic shift for each ligand position, except for 4-CH_3 and 7-H, where π-contact shifts dominate.

For the remaining ligand protons, where both σ-contact and dipolar interactions are operative, the resonance spread generally has the order 2,9-H > 3,8-H ~ 5,6-H, which is consistent with the relative magnitudes of both the σ-contact and the dipolar interactions at those positions. That the magnetic inequivalence of the eight 2,9-H, 3,8-H, and 5,6-H peaks is more likely to arise from differences in the dipolar interaction than in the σ-contact interaction is strongly supported by a comparison with the analogous Ni(II) chelates, whose contact shifts for the 4-phen and 3,4-phen ligand are also included in Table VI. Thus for the magnetically isotropic Ni(II) compounds, no splittings are observed for the 3,8-H, while the Co(II) chelate showed a spread of 8.7 ppm. The ~450-Hz (at 100 MHz) 3,8-H line width for Ni(II) is nearly identical with that of the symmetric ligand; thus the inherent line width cannot mask splittings greater than ~1–2 ppm. For 5,6-H, $(4\text{-phen})_3Ni^{2+}$ does display two peaks, separated by 1.2 ppm, but this splitting is much smaller than for the analogous Co(II) chelate (4.93 ppm) and can arise from the inequivalence of the 5-H and 6-H in the uncoordinated ligand. The

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(22) G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964); W. D. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

(23) M. Wicholas and R. S. Drago, *ibid.*, **90**, 6964 (1968).

(24) W. D. Horrocks, Jr., *Inorg. Chem.*, **9**, 690 (1970).

(25) M. Wicholas and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 2196 (1968).

2,9-H line width in the Ni(II) complex is too great (>1000 Hz at 100 MHz) to yield useful information on magnetic dissymmetry. It is therefore concluded that the *direct* σ delocalization is fairly insensitive to the molecular dissymmetry.

Even for the π-dominated 4-CH_3 and 7-H shifts in the Ni(II) chelates, where the line widths are only ~80 and ~100 Hz, respectively, no evidence for splittings of the resonances is found between −60 and 100°. It is not even possible to obtain direct evidence for the presence of both isomers from the nmr data, although it is considered unlikely that the statistical mixture is not formed for the Ni(II) complexes. Furthermore, fast *cis* → *trans* isomerization can be discounted, inasmuch as it has been shown that optical racemization of $(phen)_3Ni^{2+}$ is very slow,[26] with $k \approx 10^{-3}$ sec^{-1}.

It is therefore concluded that, since the direct σ-contact interaction in the Ni(II) chelates is insensitive to the molecular dissymmetry, the sizable magnetic dissymmetry experienced by the ligand protons in the Co(II) complexes in all likelihood arises from differences in the dipolar interaction. It is not difficult to envisage the dipolar interaction affecting differently the three ligands in the *trans* isomer, inasmuch as the *trans* isomer will possess only a rhombic *g* tensor,[22] whose axes are very unlikely to coincide with those of the parent trigonal complex. This shift of the *g*-tensor axes away from the molecular symmetry axes will alter the geometric factors of a given ligand proton differently in the three ligands, *without* necessarily altering the relative orientations of the ligand protons.[27] Last, an interpretation of the anomalous temperature dependence of the isotropic shifts and of the magnitude of the resonance spread for a ligand proton in the Co(II) complexes is consistent with a dipolar origin for the differences in isotropic shifts between the isomers and between the different ligands within the *trans* isomer.[17]

π-Spin Delocalization.—The lack of any splittings of the presumably π-contact shifts for 4-CH_3 and 7-H in $(4\text{-phen})_3Ni^{2+}$ and $(3,4\text{-phen})_3Ni^{2+}$ is unexpected, since for each of the other metal ions, the π shifts were the most sensitive to the molecular dissymmetry. This apparent anomaly could arise from the fact that the 4,7 π shifts do not arise from Ni–ligand π delocalization, which would not be surprising, since octahedral Ni(II), unlike the other metal ions of interest here, does not possess any unpaired t_{2g} π-bonding d electrons. Although in lower than cubic symmetry the σ-bonding e_g orbitals are capable of interacting directly with ligand π orbitals, it is not known whether the overlap is sufficient to produce observable π-contact shifts in the ligand.

The downfield 4-H and upfield 4-CH_3 π-contact shifts are observed for both the phen and bipy chelates of Ni(II).[23] These two ligands are structurally very similar, and the energies of their highest bonding (HBO) and lowest antibonding (LAO) orbitals are also similar,[1] such that, *a priori*, spin delocalization into ligand π MO's of similar energies are expected for both ligands. The great similarity of the two ligands is exemplified by the fact that the σ-contact shifts for similarly situated protons are nearly the same[19,25] in bipy and phen. However, Hückel MO calculations, incorporating correlation by the method of McLachlan,[28] have shown that the C_4 spin density for the HBO in phen is *positive*, while the HBO C_4 spin density in bipy is negative. Thus only the bipy complex is consistent with delocalization into the HBO.

An additional, more concrete illustration of the anomalous origin of π-spin density in pyridine-type ligands attached to nickel is found in the secondary π shifts at the 4 position in octahedral Ni(II) complexes containing pyridine.[29] The observed downfield 4-H and upfield 4-CH_3 contact shifts in all cases indicate a negative C_4 π-spin density, as in the bipy[25] and phen[9] chelates. The calculated Hückel spin densities[30] for pyridine are given in Table VII, which clearly show that the negative C_4 spin density could be rationalized by direct delocalization only into ψ_3 (HBO) or one of the high-energy vacant MO's, ψ_5, since only for those orbitals can correlation effects induce the required negative C_4 spin density. However, inasmuch as both ψ_3 and ψ_5 have nodes through the bonding nitrogen, neither orbital has a component on the nitrogen, and thus both orbitals are incapable of directly or indirectly accepting spin density by virtue of symmetry considerations. Thus the 4-position π shifts in pyridine *must* arise from some indirect polarization mechanism, and due to the similarity of the π shifts in all three heterocyclic ligands of interest here, it is possible that the same indirect mechanism is operative in all these Ni(II) complexes.

TABLE VII

HÜCKEL SPIN DENSITIES FOR PYRIDINE[a]

	ψ_1 $(2.107\beta)^b$	ψ_2 (1.167β)	ψ_3 (1.00β)	ψ_4^* (-0.841β)	ψ_5^* (-1.00β)	ψ_6^* (-1.934β)
N_1	0.2705	0.3255	0.000	0.2975	0.000	0.1042
C_2	0.1753	0.0363	0.250	0.1340	0.250	0.1544
C_3	0.1303	0.1217	0.250	0.0567	0.250	0.1910
C_4	0.1175	0.3570	0.000	0.3200	0.000	0.2039

[a] $\alpha = \alpha_N + 0.5\beta$; $\beta_{CN} = \beta$. [b] Orbital energies are given in parentheses.

Two polarization mechanisms can be considered as likely sources of the anomalous "π" spin density. In one case, the relatively large unpaired spin density in the nitrogen 2s orbital (as a result of σ bonding) could cause unpairing of a filled π MO by exchange polariza-

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(26) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 232 (1949).

(27) A simple test calculation shows that the axial geometric factor, $(3 \cos^2 \chi - 1)r^{-3}$, for 2,9-H, changes by ~25% if the magnetic axis is shifted only 5° from the C_3 axis, which could readily account for the magnitudes of the observed 2,9-H resonance spread in the 4,6-phen complex, for example. The rhombic geometric factor, $\sin^2 \chi \cos 2\Omega/r^3$, has approximately the same magnitude as the axial geometric factor, depending on the location of the rhombic axes. Thus a rhombic *g*-tensor anisotropy of only 10–15% of the axial anisotropy could also produce the observed resonance spread due to different dipolar shifts.

(28) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(29) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963); R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **88**, 1071 (1966); D. Forster, K. Moedritzer, and J. R. Van Wazer, *Inorg. Chem.*, **7**, 1138 (1968).

(30) The Hückel parameters used are $\alpha_N = \alpha + 0.5\beta$ and $\beta_{CN} = \beta$.

tion in the same manner as the mechanism usually invoked to explain nitrogen hyperfine splittings in the esr spectra of aromatic free radicals.[31] Alternatively, an exchange polarization interaction between the unpaired e_g spins and the filled t_{2g} electrons[19] could cause some unpairing which must lead to a delocalization of a net negative spin density into the ligand π system. In view of the lack of sensitivity of the observed[4,7] "π" shifts to the reduced ligand symmetry, although the π shifts in the Cr(II) and Fe(III) chelates were the most sensitive to methyl substitution, the former mechanism may be dominant, since this does not necessitate postulating any metal–ligand π bonding at all.[32]

Acknowledgments.—We are indebted to Dr. E. E. Genser for attempting to obtain esr spectra of some of the Cr(II) chelates.

[31] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 6.

[32] NOTE ADDED IN PROOF.—Recent theoretical considerations (R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, in press) have shown that the dipolar shift is related to the magnetic susceptibility anisotropy and is thus *independent* of the signs of the components of the g tensor. Thus DeSimone and Drago[7] overestimated the dipolar shifts for their Fe(III) chelates by 55% using the wrong signs. The correct calculation reduced the dipolar contribution so that the contact shifts at only the 4,4′ position exhibit the sign reversal between proton and methyl group; these contact shifts are therefore inconsistent with π-spin density alone. Similarly, the dipolar shifts in our Table V are also reduced by 55% and are thus secondary to contact shifts at all positions. Moreover, as pointed out by Horrocks[24] and McGarvey (private communication), second-order Zeeman, SOZ, contributions to the dipolar shift must also be included since they are of comparable magnitude, though perhaps of opposite sign, to the first-order terms, on which basis eq 9 in ref 7 is based. Thus Horrocks (private communication) has shown that for the isoelectronic d^5 $Fe(CN)_6^{3-}$ chromophore, inclusion of SOZ terms reduces the calculated dipolar shifts to one-fifth their value obtained on the basis of eq 9 in ref 7. This same situation is very likely to obtain in the present d^5 Fe(III)–bipy chelates.[7] Pending a more detailed and correct analysis of the dipolar shifts in these Fe(III) chelates, DeSimone and Drago's conclusions on the relative importance of dipolar shifts and the unimportance of σ-spin delocalization cannot be considered even qualitatively valid. On the other hand, a possible overestimation of the dipolar shifts for the Fe(III) chelates does not affect the necessarily qualitative conclusions of the present article.

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The Effect of Ring Size on the Stability of Polyamine Complexes Containing Linked Consecutive Rings

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Equilibrium constants are determined for the protonation and metal complexation of N,N-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) and N-(2-aminoethyl)-1,3-propanediamine (2,3-tri). In the 1:1 complexes the 5,6,5-membered chelate ring system forms more stable complexes than 5,5,5-membered rings by factors of $10^{3.8}$, $10^{2.0}$, and $10^{0.7}$ for Cu(II), Ni(II), and Zn(II), respectively. The 5,6-membered chelate ring system forms 1:1 complexes with nickel of the same stability as 5,5-membered rings. The log K values for the protonation constants are 10.25, 9.50, 7.28, and 6.02 for 2,3,2-tet and are 10.03, 9.11, and 6.18 for 2,3-tri (25.0° and $\mu = 0.5\ M$). The formation constants for the complexes $M(2,3,2\text{-tet})^{2+}$ (M = Ni, Cu, Zn) are log K = 16.4, 23.9, and 12.8, respectively. Nickel also forms a complex $Ni(2,3,2\text{-tet})_2^{2+}$ with log $\beta_2 = 20.1$. The formation constants for the nickel complexes of 2,3-tri are log $K_1 = 10.7$ and log $\beta_2 = 17.8$.

Introduction

Recently a number of investigators[2–4] have reported complexes of the quadridentate ligand N,N′-bis-(2-aminoethyl)-1,3-propanediamine (2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$). The complexes of this ligand with metal ions exhibit striking differences in properties compared to the well-known trien, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, complexes. These differences have been attributed to steric constraints in the three linked 5-membered rings of trien which are relieved by the presence of a 6-membered ring in the 2,3,2-tet complexes. It was of interest to see how the balance between the relief of ring strain and the unfavorable effects due to the presence of a 6-membered ring would be reflected in the stability constants of the 2,3,2-tet complexes.

In the present work the formation constants of the 2,3,2-tet complexes of Ni(II), Cu(II), and Zn(II) and the N-(2-aminoethyl)-1,3-propanediamine (2,3-tri), $H_2N(CH_2)_2NH(CH_2)_3NH_2$, complexes of Ni(II) were measured. The 2,3,2-tet complexes are more stable than the corresponding trien complexes and the 1:1 2,3-tri complex has the same stability as the 1:1 dien, $H_2N(CH_2)_2NH(CH_2)_2NH_2$, complex, but the 2:1 complex is less stable than the corresponding dien complex.

Experimental Section

Reagents.—Nickel sulfate (reagent grade) was recrystallized twice from water and standardized by the addition of excess *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate and back-titration with standard calcium chloride solution using methyl thymol blue indicator. Copper perchlorate was prepared from copper carbonate and perchloric acid and was recrystallized before use. Zinc perchlorate was recrystallized three times from water and standardized by EDTA titration using Erio-

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