CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF QUEENSLAND, BRISBANE, QUEENSLAND, AUSTRALIA

Complexes with Six-Membered Chelate Rings. II. Proton Magnetic Resonance Study of Trimethylenediamine, Some Methyl-Substituted Derivatives, and Their Complexes with Platinum(II) and Palladium(II)

BY T. G. APPLETON AND J. R. HALL

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Pmr spectra of compounds (diamine)$(HCl)_2$, M(diamine)$_2^{2+}$, and M(diamine)$(NH_3)_2^{2+}$ are reported, where M = Pt(II), Pd(II); diamine = trimethylenediamine, 2-methylpropane-1,3-diamine, pentane-2,4-diamine, neopentanediamine, ethylenediamine, *meso*-butane-2,3-diamine. These spectra are discussed in terms of the conformational behavior of the chelate rings. An unusual Pt–H coupling over four saturated bonds is observed in some complexes.

Introduction

There have been some pmr studies on metal–diamine complexes,[1-9] but these have been almost exclusively on octahedral complexes of ethylenediamine and its derivatives. In all six-coordinate complexes there must be a group attached to the metal ion "axial" to the chelate ring. It seemed desirable to study complexes with metal ions having square-planar coordination, such as platinum(II) and palladium(II), where the chelate ring is as free as possible from interactions with any other groups attached to the central ion. Because of the possible analogy in the conformational behavior between six-membered rings formed when trimethylenediamine and derivatives chelate to a metal ion and the corresponding cyclohexane derivatives, we have studied the pmr spectra of a number of complexes of Pt(II) and Pd(II) with trimethylenediamine and some methyl-substituted derivatives. Some complexes containing five-membered chelate rings were also studied for comparison with the six-membered ring systems. Few pmr spectra of trimethylenediamine complexes have been reported.[3] A recent communication[10] has some relevance to this work. It was reported that in (−)-propylenediamine complexes with Pt(II) and Pd(II) the chelate ring took up the expected λ-*gauche* conformation and that in certain Pt(II), Pd(II), and Co(III) complexes with *meso*-butane-2,3-diamine, *meso*-stilbenediamine, and isobutylenediamine the conformational inversion was rapid on the nmr time scale.

Experimental Section

Preparation of compounds is described in the preceding paper.

N-Deuteration and Deuterated Solvents.—N-Deuteration of a complex was carried out by dissolving it in D_2O, allowing the solution to stand for several hours, and then evaporating to dryness in a vacuum desiccator over phosphorus(V) oxide. This process was then repeated.

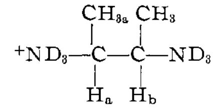
D_2O was 99% deuterated. Dimethyl sulfoxide-d_6 (DMSO-d_6) (99.5%), methanol-d_4, and acetone-d_6 were obtained from Fluka. DCl solution was prepared by passing gaseous DCl, produced by the action of D_2O on benzoyl chloride, through D_2O.

Spectra.—Nmr spectra were run on a Varian A-60 spectrometer with a V-6040 variable-temperature attachment. Heteronuclear spin decoupling was carried out on [Pt(*meso*-dptn)$_2$]Cl_2 with the apparatus described by Banney, *et al.*[11] Spectra were run with *t*-butyl alcohol as internal standard. Chemical shift data are reported on a τ' scale (relative to DSS, 2,2-dimethyl-2-silapentane-5-sulfonate) using τ' 8.769 for *t*-C_4H_9OH in D_2O.[12] The 100-MHz spectra were run by Dr. S. R. Johns, Division of Applied Chemistry, CSIRO, on a Varian HA-100 spectrometer.

Results

Pmr Spectra of N-Deuterated Compounds in D_2O. Ethylenediamine Compounds.—(en)$(HCl)_2$[13] in D_2O gives a single sharp peak (Table I). In the dihydrochlorides the NH protons exchange rapidly with solvent deuterium and have no effect on the spectrum. N-Deuterated [Pd(en)$_2$]Cl_2 in D_2O also shows a single, sharp peak. As previously reported,[1,14] N-deuterated [Pt(en)$_2$]Cl_2 gives a sharp peak together with "satellite" peaks due to coupling with ^{195}Pt ($I = 1/2$, 34% abundance). N-Deuterated [Pt(en)$(NH_3)_2$]Cl_2 has a similar spectrum.

***meso*-Butane-2,3-diamine Compounds.**—(*meso*-bn)$(HCl)_2$ in D_2O shows a doublet ($J_{CH-CH_3} = 6.5$ Hz) at τ' 8.57 corresponding to the six protons of the methyl groups and a quartet at τ' 6.32 corresponding to the two >C*H*–CH_3 protons. Each peak of the methine quartet is split by 2 Hz. This may be because $J_{H_a-CH_{3a}} \neq J_{H_b-CH_{3a}}$. H_a and H_b then may not be "equivalent in the coupling constant sense."[15] N-Deuterated [Pt-



$$^{+}ND_3-\underset{H_a}{\overset{CH_{3a}}{C}}-\underset{H_b}{\overset{CH_3}{C}}-ND_3^{+}$$

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[1] D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 791 (1959).

[2] S. T. Spees, L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966).

[3] H. Yoneda and Y. Morimoto, *Bull. Chem. Soc. Jap.*, **39**, 2180 (1966).

[4] R. C. Henney, H. F. Holtzclaw, and R. C. Larson, *Inorg. Chem.*, **5**, 940 (1966).

[5] I. R. Lantzke and D. W. Watts, *Aust. J. Chem.*, **20**, 35 (1967).

[6] D. A. Buckingham, L. Durham, and A. M. Sargeson, *ibid.*, **20**, 257 (1967).

[7] B. M. Fung, *J. Amer. Chem. Soc.*, **89**, 5788 (1967).

[8] H. Elsbernd and J. K. Beattie, *ibid.*, **91**, 4573 (1969).

[9] T. G. Appleton, J. R. Hall, and C. J. Hawkins, *Inorg. Chem.*, **9**, 1299 (1970).

[10] S. Yano, H. Ito, J. Fujita, and K. Saito, *Chem. Commun.*, 460 (1969).

[11] P. J. Banney, D. C. McWilliam, and P. R. Wells, to be submitted for publication.

[12] R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, 3739 (1964).

[13] For all abbreviations, see the preceding paper, footnote 6.

[14] A. F. Eidson and C. F. Liu, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., 1968, No. INOR 83.

[15] M. von Gorkom and G. E. Hall, *Quart. Rev., Chem. Soc.*, **22**, 14 (1968).

TABLE I
ETHYLENEDIAMINE AND NEOPENTANEDIAMINE COMPOUNDS

Compound	τ' (methylene)	Width[a] (methylene), Hz	$J_{\text{Pt-N-C-H}}$, Hz	τ' (methyl)	Width[a] (methyl), Hz
$(en)(HCl)_2$	6.57	1.0	...	...	...
$[Pd(en)_2]Cl_2$	7.25	2.0	...	...	...
$[Pt(en)_2]Cl_2$	7.34	2.0	41.0	...	...
$[Pt(en)(NH_3)_2]Cl_2$	7.34	1.5	41.5	...	...
$(dan)(HCl)_2$	6.98	1.0	...	8.84	1.0
$[Pd(dan)_2]Cl_2$	7.64	2.0	...	9.06	1.0
$[Pt(dan)_2]Cl_2$ $[Pt(dan)(NH_3)_2]Cl_2$	7.54	2.0	40.5	9.06	1.0

[a] Width at half-height.

(*meso*-bn)$(NH_3)_2]Cl_2$ shows a doublet at τ' 8.74 corresponding to the methyl group protons ($J_{\text{CH-CH}_3}$ = 6.5 Hz). The methine proton absorption is complicated by coupling with ^{195}Pt. No value of $J_{\text{Pt-N-C-H}}$ could be obtained.

Trimethylenediamine Compounds.—The spectrum of $(tn)(HCl)_2$ in D_2O is reproduced in Figure 1. A multiplet centered at τ' 6.93 corresponds to the four protons of the outer methylene groups and a multiplet at τ' 7.92 to the two protons of the inner methylene group. Although these multiplets are roughly a triplet and quintet, respectively, there is considerable fine structure in the spectrum, particularly in the inner methylene group resonance. This fine structure remained essentially unchanged in a spectrum run at 100 MHz. Although H_a and H_b are chemically equivalent, $J_{H_a-H_c} \neq J_{H_b-H_c}$ in the conformation which would probably be preferred

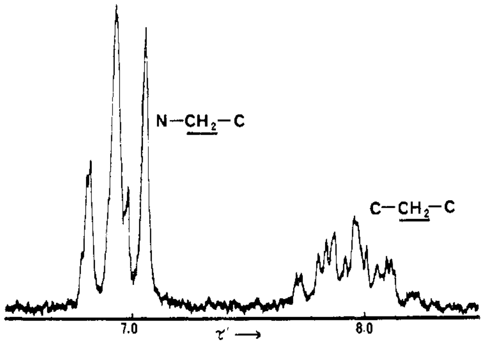
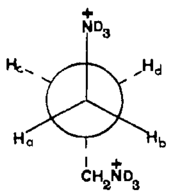


Figure 1.—The 60-MHz pmr spectrum of trimethylenediamine dihydrochloride in D_2O.



Unless all three possible rotamers are equally populated, a complex $(AA')_2BB'$ spectrum would be expected.[15,16] From the splitting of the "triplet" peaks, $J_{\text{CH}_2\text{-CH}_2}$ is approximately 7.5 Hz. 1,3-Dibromopropane, propane-1,3-diol, and free trimethylenediamine in D_2O all give spectra very close to a simple triplet–quintuplet pattern. The preference for the symmetrical rotamer must be less for these molecules.

The spectra of N-deuterated $[Pd(tn)_2]Cl_2$, $[Pt(tn)_2]Cl_2$, and $[Pt(tn)(NH_3)_2]Cl_2$ in D_2O are rather similar to that of $(tn)(HCl)_2$, except that, in the platinum complexes, coupling with ^{195}Pt gives rise to an additional triplet on each side of the outer methylene group signal ($J_{\text{Pt-N-C-H}}$ = 43 Hz). The spectra of the two platinum complexes are similar, apart from greater intensities in the complex with two chelate rings, with the multiplets centered at τ' 7.23 and 8.27. In the palladium complex they occur at τ' 7.28 and 8.24, respectively. The approximate value for $J_{\text{CH}_2\text{-CH}_2}$ in these complexes is 5.5 Hz.

2-Methylpropane-1,3-diamine Compounds.—There are three multiplets in the spectrum of $(metn)(HCl)_2$ in D_2O (Figure 2): a complex multiplet at τ' 6.95 corresponding to the four protons of the methylene groups; a multiplet at τ' 7.77 corresponding to the $>CH\text{-}CH_3$ proton; a doublet at τ' 8.86 corresponding to the three protons of the methyl group ($J_{\text{CH-CH}_3}$ = 6.5 Hz). The methylene group protons are chemically nonequivalent. In none of the possible conformations about the C–C bond can H_a be equivalent to H_b

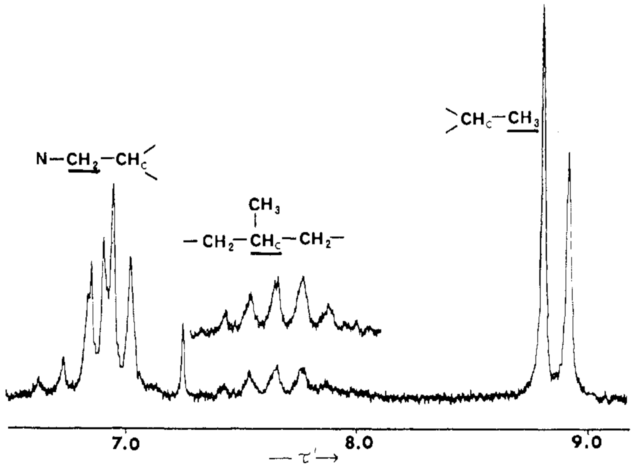
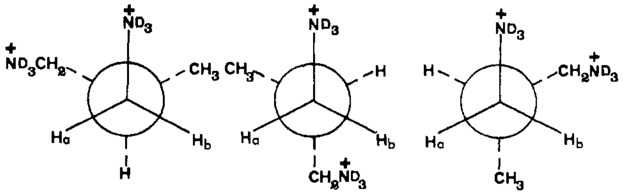


Figure 2.—The 60-MHz pmr spectrum of 2-methylpropane-1,3-diamine dihydrochloride in D_2O.



Thus, the methylene group protons represent the AB part of an $(AB)_2C$ spectrum. Similar cases are discussed by von Gorkom and Hall.[15] Approximate analysis of the eight-line pattern gives the coupling constants: $|J_{AC}|$ = 6.3 Hz, $|J_{BC}|$ = 7.7 Hz, $|J_{AB}|$ = 12.5 Hz, $\Delta\nu_{AB}$ = 12.3 Hz. The near-equality of the three coupling constants involving H_C gives rise to a relatively simple multiplet for this proton.

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(16) M. L. Martin and G. J. Martin, *Bull. Soc. Chim. Fr.*, 2117 (1966).

TABLE II
PENTANE-2,4-DIAMINE COMPOUNDS

Compound	τ' (methine) H_X	τ' (methylene) H_A	τ' (methylene) H_B	τ' (methyl)	$\lvert J_{AB}\rvert$, Hz	$\lvert J_{AX}\rvert$, Hz	$\lvert J_{BX}\rvert$, Hz	$J_{CH_X-CH_3}$, Hz
(*meso*-dptn)$(HCl)_2$	6.41	7.89	8.14	8.62	15.0	6.8	7.8	6.5
[Pd(*meso*-dptn)$_2$]Cl_2	7.05	8.20	8.83	8.85	15.5	2.5	11.0	6.5
[Pt(*meso*-dptn)$_2$]Cl_2 [Pt(*meso*-dptn)$(NH_3)_2$]Cl_2	6.98	8.15	8.78	8.83	15.0	2.3	11.0	6.5
((±)dptn)$(HCl)_2$	6.45	8.00	...	8.64	...	7.5	...	6.5
[Pd((±)dptn)$_2$]Cl_2	6.86	8.35	...	8.66	...	5.5	...	6.5
[Pt((±)dptn)$_2$]Cl_2 [Pt((±)dptn)$(NH_3)_2$]Cl_2	6.89	8.28	...	8.68	...	5.5	...	6.5

In the spectrum of N-deuterated [Pt(metn)$(NH_3)_2$]Cl_2 in D_2O a doublet is observed in the methyl group region at τ' 9.15. The other two signals overlap, and no coupling constants involving the methylene group could be obtained.

Neopentanediamine Compounds.—(dan)$(HCl)_2$ and [Pd(dan)$_2$]Cl_2 each give two sharp peaks, corresponding to the four protons of the methylene groups and the six protons of the methyl groups (Table I). The spectra of N-deuterated [Pt(dan)$_2$]Cl_2 and [Pt(dan)$(NH_3)_2$]Cl_2 contain the additional feature of "satellites" about the methylene group signal from coupling with ^{195}Pt. There is no observable coupling between ^{195}Pt and the methyl group protons.

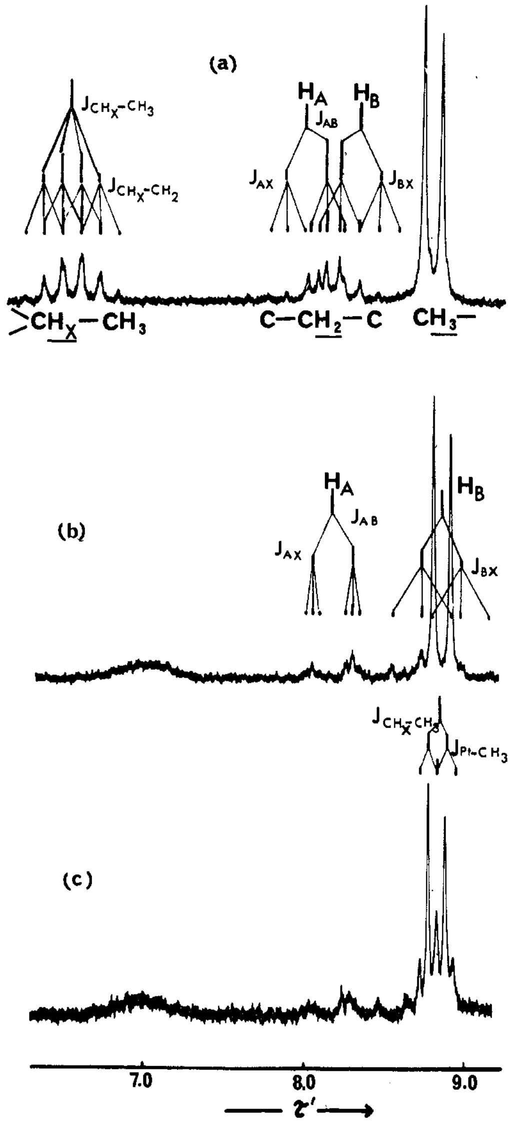

Figure 3. The 60-MHz pmr spectra of *meso*-pentane-2,4-diamine compounds in D_2O: (a) (*meso*-dptn)$(HCl)_2$; (b) N-deuterated [Pd(*meso*-dptn)$_2$]Cl_2; (c) N-deuterated [Pt(*meso*-dptn)$_2$]Cl_2.

Pentane-2,4-diamine Compounds.—The spectrum of (*meso*-dptn)$(HCl)_2$ in D_2O is reproduced in Figure 3a. The two methylene protons are nonequivalent (the sole molecular symmetry element, the mirror plane, is coincident with the H_M–C–H_N plane (Figure 4a)). These protons couple to the two equivalent methine protons, so that the methylene group pattern corresponds to the AB part of an ABX_2 spectrum, analysis of which gave the coupling constants in Table II. The similarity of the three coupling constants involving H_X causes this proton to give a sextet, with some secondary splitting.

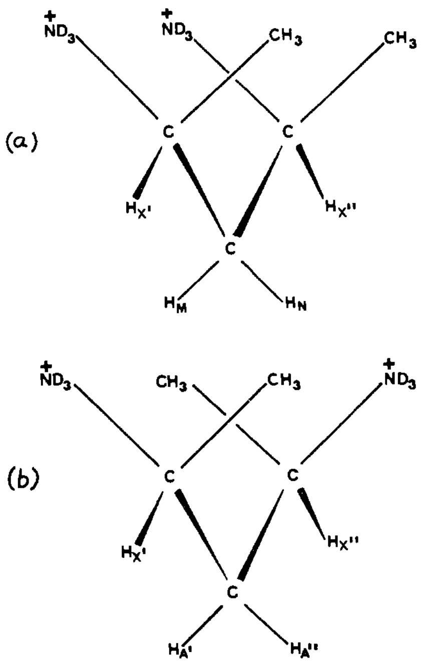

Figure 4.—(a) *meso*-Pentane-2,4-diamine. (b) (±)-Pentane-2,4-diamine.

The spectrum of N-deuterated [Pd(*meso*-dptn)$_2$]Cl_2 is reproduced in Figure 3b. The H_X resonance is a broad, unresolved band. The methylene group pattern is spread over a greater width than in the ligand dihydrochloride and partially overlaps the methyl signal.

This pattern was analyzed once again as the AB part of an ABX_2 spectrum (Table II).

The spectrum of N-deuterated $[Pt(\textit{meso}\text{-dptn})_2]Cl_2$ is reproduced in Figure 3c. The methine and methylene resonances are essentially similar to those of the palladium complex (Table II). No value for $J_{Pt-N-C-H_X}$ could be obtained. The spectrum differs from that of $[Pd(\textit{meso}\text{-dptn})_2]Cl_2$ in that there is an additional triplet (spacing 6.5 Hz, intensity ratio 1:2:1) superimposed symmetrically on the methyl doublet. The total intensity of the triplet corresponds, at least approximately, to one-third of the total intensity of doublet plus triplet. The spectra of $[Pt(\textit{meso}\text{-dptn})(NH_3)_2]Cl_2$ and $[Pt(\textit{meso}\text{-dptn})(NH_3)_2](ClO_4)_2$ in D_2O are similar to that of the bis-diamine complex. In the 100-MHz spectrum of $[Pt(\textit{meso}\text{-dptn})(NH_3)_2]Cl_2$, the spacing within the overlapping doublet–triplet remains unchanged. When the sample is exposed to intense radiation of frequency ~12.9 MHz, corresponding to the resonance frequency of ^{195}Pt, the triplet pattern disappears. Thus, the additional triplet must arise from coupling of the methyl protons with ^{195}Pt, two lines coinciding at the central peak of the triplet because of the accidental equality of the values of $J_{CH_X-CH_3}$ and $J_{Pt-N-C-C-H}$.

The spectrum of $((\pm)\text{dptn})(HCl)_2$ in D_2O is reproduced in Figure 5a. As the diamine dihydrochloride is capable of existing in conformations such as that depicted in Figure 4b, where there is a C_2 axis through the central carbon atom bisecting the $H_{A'}-C-H_{A''}$ angle, $H_{A'}$ is chemically equivalent to $H_{A''}$. Further, $J_{H_{A'}-H_{X'}} = J_{H_{A''}-H_{X'}} = J_{H_{A'}-H_{X''}} = J_{H_{A''}-H_{X''}}$, so that $H_{A'}$ and $H_{A''}$ are completely equivalent magnetically. This is reflected in the relatively simple methylene resonance of the racemic isomer, a triplet. The slight upfield shift of the methyl doublet in the racemic isomer relative to the *meso* isomer (Table II) makes nmr a sensitive method for determining the relative proportions of the two isomers in any sample of $(\text{dptn})(HCl)_2$. The similarity of the two coupling constants involving H_X gives rise to a six-line multiplet for this proton, with splitting 7.0 Hz.

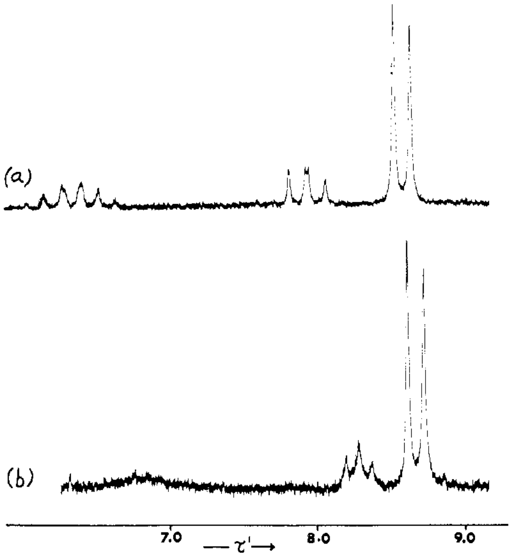

Figure 5.—The 60-MHz pmr spectra of (±)-pentane-2,4-diamine compounds in D_2O: (a) $((\pm)\ \text{dptn})(HCl)_2$; (b) N-deuterated $[Pt(\pm)\text{dptn})(NH_3)_2](ClO_4)_2$.

The spectrum of $[Pt((\pm)\text{dptn})(NH_3)_2](ClO_4)_2$ in D_2O is reproduced in Figure 5b. The spectrum of the chloride salt is identical. At high amplification, or when run with a time-averaging computer, the H_X signal is resolved into a multiplet containing four central peaks (splitting 5.8 Hz) and various weaker peaks, some presumably arising from coupling with ^{195}Pt. No Pt–N–C–H coupling constant could be measured. There is no coupling between ^{195}Pt and the methyl protons.

The spectrum of $[Pt((\pm)\text{dptn})_2]Cl_2$ at 60 MHz is similar to that of $Pt((\pm)\text{dptn})(NH_3)_2^{2+}$ (both N deuterated) (Table II), except that the methyl doublet is very slightly split (≤ 1 Hz). The spectrum of $[Pd((\pm)\text{dptn})_2]Cl_2$ is similar to that of the platinum complex, with slightly better resolution of the H_X resonance into six lines, as there is now no coupling with the metal ion. Again, there is a slight splitting of the methyl doublet. At 100 MHz, the splitting is more apparent (1.8 Hz) (Figure 6). A similar splitting occurs in the methylene group triplet, but the H_X signal does not appear to be affected. Some additional peaks are present on the downfield side of the methylene signal to 100 MHz.

Variable-Temperature Studies.—In D_2O, perchlorate salts, $[Pt(\text{diamine})(NH_3)_2](ClO_4)_2$, gave spectra identical with those of the chloride salts, but, unlike the chlorides, they are soluble in a range of solvents, enabling variable-temperature studies to be extended to higher or lower temperatures than those available with aqueous solutions. Spectra of N-deuterated complexes in methanol-d_4, acetone-d_6, and DMSO-d_6 at 30° were similar to those in D_2O at 30°. In some cases, the methyl region only was studied in methanol, ethylene glycol, or glycol–water mixtures. $t\text{-}C_4H_9OH$ or chloroform was used an internal reference.

Raising the temperature has no observable effect on the spectra (apart from the usual falloff in signal to noise ratio, due to increased population of the excited nuclear spin states[17]). For example, up to 167° in DMSO-d_6 the five-line pattern in the methyl region of $[Pt(\textit{meso}\text{-dptn})(NH_3)_2](ClO_4)_2$ does not change.

On cooling below −50° in methanol or acetone, broadening occurs in all of the signals in N-deuterated complexes of the type $[Pt(\text{diamine})(NH_3)_2](ClO_4)_2$, although the reference signal remains sharp. This broadening continues as the temperature is lowered to the vicinity of −100°. In glycol–water or DMSO-d_6–D_2O the signals have broadened out by −35°. The solvent is very viscous at these temperatures, and on further cooling freezes to a "glass." The reference $t\text{-}C_4H_9OH$ signal also broadens, though much less than the peaks from the complex.

Spectra of Undeuterated Complexes in D^+–D_2O.—

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(17) G. E. Hall, *Ann. Rev. NMR Spectrosc.*, **1**, 227 (1968).

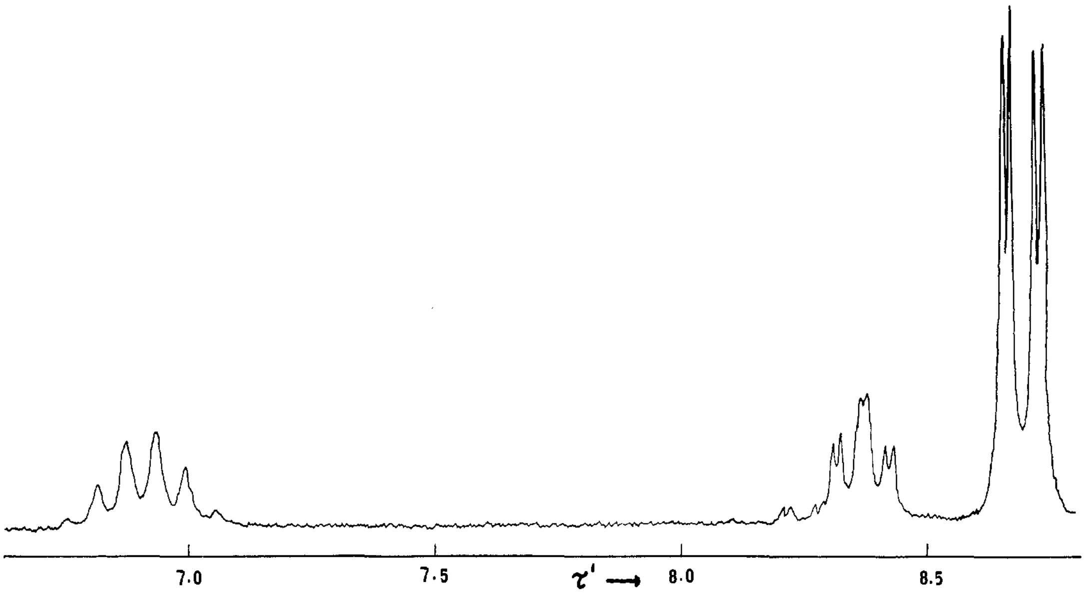
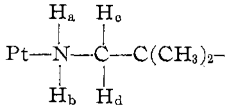


Figure 6.—The 100-MHz pmr spectrum of [Pd ((±) dptn)$_2$]Cl$_2$.

The rate of exchange of protons attached to nitrogen with deuterons from the aqueous solvent decreases as the solution becomes more acid. The rate of N-deuteration of platinum(II) complexes in solutions of D_2O acidified with DCl or D_2SO_4 is sufficiently slow for spectra of undeuterated complexes to be obtained in these solvents. This technique cannot be applied to bis(diamine)palladium complexes, which decompose in acid solution.

In general, the presence of N–H protons complicates the spectra of protons attached to neighboring carbon atoms by coupling. When the spectrum of such CH atoms is already fairly complicated in the N-deuterated complexes, little can be deduced from the more complex spectrum when NH protons are present, but where the spectrum of the deuterated complex is simple, some comments are worthwhile.

The methylene region of the spectrum of [Pt(dan)$_2$]Cl$_2$ in DCl solution is reproduced in Figure 7a. An identical spectrum is obtained in D_2SO_4 solution. The pattern is rather complex and is reproduced in the "satellites" from coupling with ^{195}Pt. The complexity arises because $J_{NH_a-CH_c} \neq J_{NH_b-CH_c}$. Thus, an AA'-



$$\mathrm{Pt{-}\underset{H_b}{\overset{H_a}{N}}{-}\underset{H_d}{\overset{H_c}{C}}{-}C(CH_3)_2{-}}$$

XX' pattern would be expected. The characteristics of such a spectrum are described by Pople, Bernstein, and Schneider.[18] A strong doublet is predicted in the methylene region, together with two symmetrical quartets whose inner lines are more intense. Not all these features can be distinguished in this spectrum, but it is probable that lines A and E represent the strong doublet, B and D the inner lines of one quartet, and two overlapping lines at C the inner lines of the other.

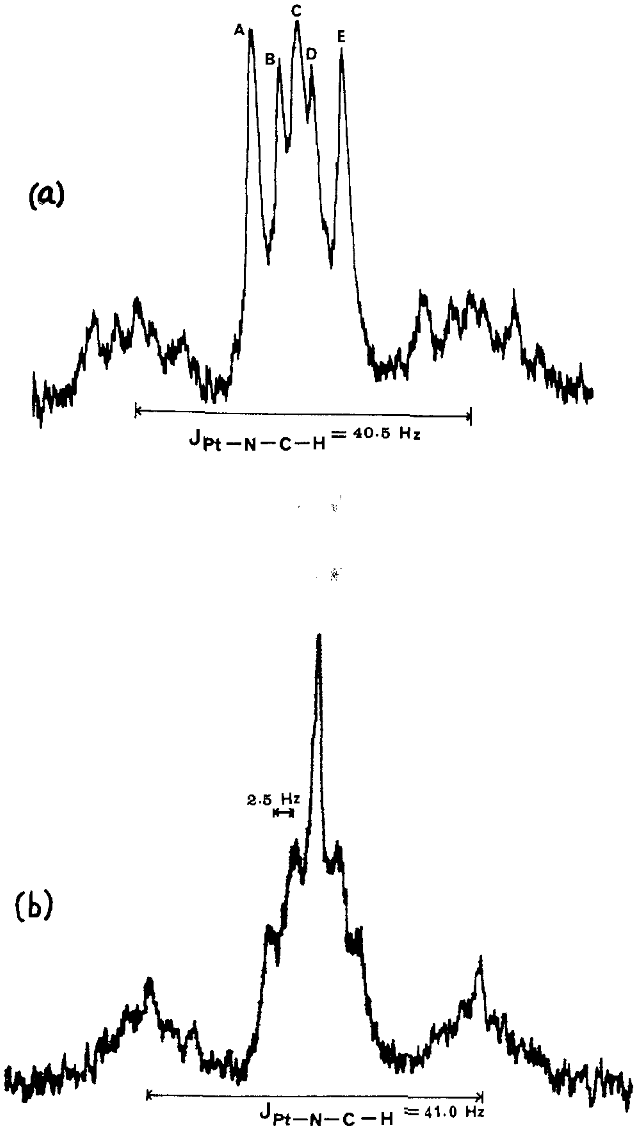


Figure 7.—The 60-MHz pmr spectra of undeuterated complexes in DCl solution: (a) methylene region of [Pt(dan)$_2$]Cl$_2$; (b) methylene region of [Pt(en)$_2$]Cl$_2$.

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[18] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 140.

The only quantity which can be obtained with any certainty from the spectrum is the spacing between the peaks of the strong doublet, $J_{\mathrm{NH_a-CH_c}} + J_{\mathrm{NH_a-CH_d}} =$ 11 Hz, so that the average value of $J_{\mathrm{NH-CH}}$ is 5.5 Hz.

The NH_2 protons give a broad signal (width 20 Hz) at τ' 5.3, with "wings" from coupling with ^{195}Pt. The broadness of the band (from interaction with the ^{14}N quadrupole) prevents accurate measurement of $J_{\mathrm{Pt-N-H}}$, but it is approximately 60 Hz.

With $[Pt(en)_2]Cl_2$, the expected nonequivalence of $J_{\mathrm{NH-CH}}$ values might be expected to give rise to a complicated $(XX')_2(AA')_2$ pattern. As shown in Figure 7b, a "quintet" is observed, which is reproduced in the "satellites." Coupling between the methylene protons is sufficiently strong for only an average coupling with all four NH protons to be observed. The pattern may be described in terms of "virtual coupling." Similar cases are discussed by Musher and Corey.[19]

The NH protons once again give a broad peak (τ' 4.87) with "wings" from coupling to ^{195}Pt ($J_{\mathrm{Pt-N-H}} =$ 60 Hz).

Discussion

Like the cyclohexane ring a six-membered chelate ring is capable of existing in two basic conformational types, "chair" conformations (Figure 8a) and flexible conformations, including the various "boat" and "skew-boat" or "twist" conformations (Figure 8b). A detailed conformational analysis of the isolated trimethylenediaminemetal ring has predicted that the conformation will be "chair" type, readily flattened about the M–N–C angles.[20] "Chair" conformations flattened about these angles have been found in the trimethylenediamine complexes that have been studied by X-ray crystallography, *viz.*, $[Co(tn)_3]Br_3$[21] (M–N–C = 117.4°), $[Ni(tn)_2(OH_2)_2](NO_3)_2$[22] (121.3°), $[Cu(tn)_2(NO_3)_2]$[23] (119.4°), and $[Co(tn)_2Cl_2]Cl$.[24] There has been little experimental information on the conformational type preferred in solution or the rate of conformational interconversion (fast on the nmr time scale for most cyclohexane derivatives at room temperature).

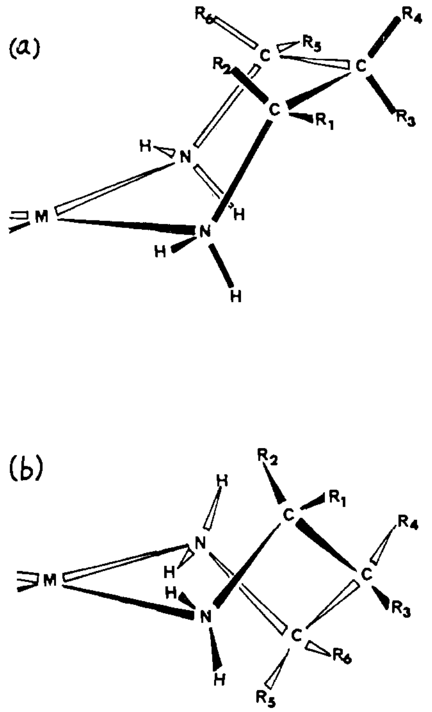

Figure 8.—Possible conformations of six-membered chelate rings: (a) chair type; (b) skew-boat type.

Complexes with Five-Membered Chelate Rings.—Our results, in agreement with those of others,[10] suggest that conformational equilibration is rapid. The methylene protons of the metal–ethylenediamine ring would be nonequivalent in any nonplanar conformation, but a sharp singlet is observed for N-deuterated complexes, consistent with averaging of the proton environments by rapid conformational inversion. This effective equivalence of the methylene protons makes the resolution of $Pt(en)_2^{2+}$ reported by Eidson and Liu[14] difficult to explain. In any fixed, puckered conformation of the *meso*-butane-2,3-diamine chelate ring the two methyl groups would be nonequivalent, one being equatorial and the other axial. The presence of only one methyl doublet in the pmr spectrum of $Pt(\textit{meso}\text{-bn})(NH_3)_2^{2+}$ again implies that conformational inversion is rapid.

Complexes with Six-Membered Chelate Rings.—The spectra of the complexes with six-membered chelate rings are all consistent with rapid conformational interconversion, and where the spectra imply a preferred conformation, this is chair type. The spectra of the trimethylenediamine complexes studied are no more complicated than the spectrum of $(tn)(HCl)_2$, suggesting rapid conformational equilibration. There are two possible chair-type conformations for chelate rings formed with 2-methylpropane-1,3-diamine: one with the methyl group equatorial ($R_4 = CH_3$, other R = H in Figure 8a) and one with the methyl group axial ($R_3 = CH_3$, other R = H in Figure 8a). These might be expected to be in equilibrium in solution, with the former predominating. Observation of only one methyl doublet is again consistent with rapid conformational interconversion at 30°.

For a neopentanediamine chelate ring in a chair-type conformation (R_3, $R_4 = CH_3$, other R = H in Figure 8a) one methyl group (R_4) would be equatorial and one (R_3) axial. The methylene protons would also be nonequivalent. In a fixed skew-boat type of conformation (R_3, $R_4 = CH_3$, other R = H in Figure 8b) the methyl groups would be equivalent but the methylene protons would not. The observation of sharp peaks in both regions of the spectra of these complexes is again consistent with rapid conformational equilibria.

meso-**Pentane-2,4-diamine Complexes.**—These spectra (Figure 3) can be explained on the basis of a strong preference for the chair-type conformation with both

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methyl groups equatorial (R_1, $R_5 = CH_3$, R_2, $R_6 = H_X$, $R_4 = H_A$, $R_3 = H_B$ in Figure 8a). Then the two H_X protons are axial, H_A is equatorial, and H_B is axial. The striking difference between J_{BX} and J_{AX} (11.0 and 2.5 Hz, respectively, in [Pd(*meso*-dptn)$_2$]Cl$_2$) can be explained in terms of the Karplus equation[12,25]

$$\begin{aligned} J_{H-C-C-H} &= k_1 \cos^2 \phi - C \qquad 0° \leqslant \phi \leqslant 90° \\ &= k_2 \cos^2 \phi - C \qquad 90° \leqslant \phi \leqslant 180° \end{aligned}$$

where ϕ is the dihedral angle between the relevant C–C–H planes, k_1 and k_2 are constants, and C is a small constant. The dihedral angle, ϕ, for H_B–H_X is close to 180°, and that for H_A–H_X is a little greater than 60°. Application of the Karplus equation then leads to the prediction $J_{BX} > J_{AX}$, as found. The values of these coupling constants are comparable with those for $J_{H_{ax}-H_{ax}}$ and $J_{H_{eq}-H_{ax}}$ in cyclohexane derivatives (6–12 Hz and 0–6 Hz, respectively).[25] The τ' values for H_A (equatorial) and H_B (axial), 8.18 and 8.86, respectively, are consistent with this interpretation, as it is usually observed that equatorial groups resonate at fields lower than for axial. A strong preference for a particular conformation does not, of course, imply that conformational equilibration is not rapid.

The alternative chair conformation, where both methyl groups are axial (R_2, $R_6 = CH_3$, other $R = H$ in Figure 8a) is inconsistent with the observed spectrum, as then both H_X would be equatorial, and the difference between J_{AX} and J_{BX} would be comparatively small. The skew-boat type of conformation is also inconsistent with the observed spectrum. There are two equivalent conformations of this type (*e.g.*, R_1, $R_5 = CH_3$, $R_2 = H_{X'}$, $R_6 = H_{X''}$, $R_4 = H_A$, $R_3 = H_B$ in Figure 8b). In each, the two methyl groups and the two H_X protons are nonequivalent. $J_{BX'}$ will then be greater than $J_{BX''}$, $J_{AX'}$, or $J_{AX''}$, but in the other skew-boat conformation $J_{BX''}$ will be greater than the other couplings. If the skew-boat conformations are then interconverting rapidly (implied by the one methyl doublet observed), an average J_{BX} would be obtained, greater, but not very much greater, than the average J_{AX}.

Long-range platinum–proton coupling over four saturated bonds, as observed in Pt(*meso*-dptn)$_2{}^{2+}$ and Pt(*meso*-dptn)(NH$_3$)$_2{}^{2+}$, has not previously been reported. It may be seen from Figure 9 that with a chair conformation with equatorial methyl groups it is possible for the bonds between the Pt atom and one of the methyl protons to take up a planar W configuration. It is well-established that H–H coupling over four saturated bonds can become significant when such a configuration occurs.[26] It has been shown that three-bond coupling constants, $J_{Pt-N-C-H}$, are analogous in their angular dependence to $J_{H-C-C-H}$.[27] A planar W configuration is not possible if the methyl group is axial. The comparative rigidity of the chair conformation may also favor this long-range coupling. No such coupling has been observed in propylenediamine complexes of platinum(II),[10] although there is a strong preference for the conformation with the methyl group equatorial, allowing a planar W configuration for the Pt–N–C–C–H bonds. An equatorial methyl group in a skew-boat conformation allows the planar W configuration, but the conformation resembles that of a five-membered ring in its flexibility. As the two skew-boat conformations in a *meso*-dptn chelate ring are equivalent, with one methyl group axial and one equatorial in each, each methyl group would be equatorial for at most 50% of the time. The long-range Pt–H coupling provides additional evidence for a strong preference for the chair conformation with equatorial methyl groups.

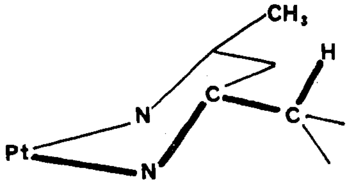

Figure 9.—Pt-*meso*-dptn chelate ring in preferred conformation.

At 60 MHz, the probable existence of the two geometric isomers and in Figure 10 has no effect on the spectrum of M(*meso*-dptn)$_2{}^{2+}$.

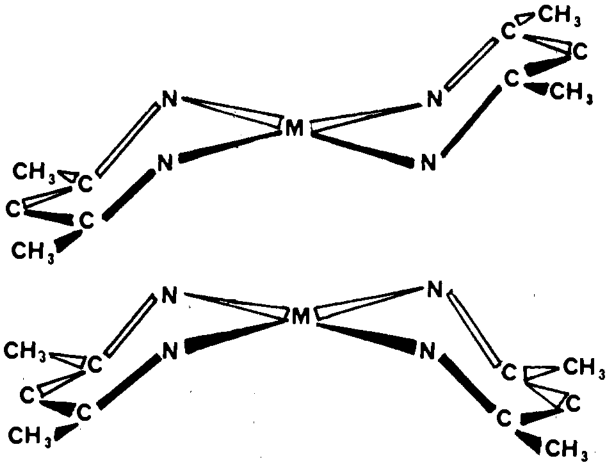

Figure 10.—Isomers of M(*meso*-dptn)$_2{}^{2+}$.

Racemic Pentane-2,4-diamine Complexes.—For these, there are two equivalent chair conformations (*e.g.*, R_1, $R_6 = CH_3$, $R_2 = H_{X'}$, $R_5 = H_{X''}$, $R_4 = H_{A'}$, $R_3 = H_{A''}$ in Figure 8a). In each, there is one equatorial methyl group (R_1) and one axial (R_6). Observation of only one methyl doublet in Pt((±)dptn)(NH$_3$)$_2{}^{2+}$ is thus consistent with rapid interconversion of chair conformations. The splitting of the methylene and methyl signals observed in the spectra of [M((±)-dptn)$_2$]Cl$_2$ probably arises from the presence of the isomers M((+)dptn)$_2{}^{2+}$, M((−)dptn)$_2{}^{2+}$, and M((+)-dptn)((−)dptn)$^{2+}$. The first two, being enantiomers, have identical spectra, which differ slightly from the spectrum of the mixed complex. If no particular combination were preferred, the concentration of the first two together would statistically be equal to that of the mixed isomer. The spectrum shows that this is so.

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Although in each conformer $H_{A'}$, $H_{A''}$, $H_{X'}$, and $H_{X''}$ are all nonequivalent, if conformational interconversion is rapid, $H_{A'}$ will become equivalent to $H_{A''}$ and $H_{X'}$ to $H_{X''}$. The additional peaks observed in the methylene region in the 100-MHz spectrum of $[Pd((\pm)dptn)_2]Cl_2$ may arise because $J_{A'X'} \neq J_{A'X''}$ in any particular chair conformation. If this conformational type is preferred, each methyl group would be in the required orientation for Pt–N–C–CH_3 coupling (*i.e.*, equatorial) for only 50% of the time, which could account for the absence of such coupling.

There are two different skew-boat conformations. In one of these (R_1, R_6 = CH_3, other R = H in Figure 8b) both methyl groups are equatorial and in the other (R_2, R_5 = CH_3) both are axial. The former would be expected to be favored over the latter, so that if the skew-boat conformation were preferred (*i.e.*, if the necessity of having one methyl group axial in the chair conformation sufficiently destabilizes it), the ring would be expected to exist almost exclusively in this conformation. Some complication of the spectrum of the methylene protons might be expected because coupling constants with the H_X protons would not all be equal.

Changes with Temperature.—The lack of significant change in the spectra on heating would be expected if conformational interconversion is already rapid at 30°. The behavior on cooling implies that conformational interchange in methanol and acetone has begun to slow down below $-50°$, but even at $-100°$ it is not sufficiently slow for spectra of individual conformers to be detected. The temperatures at which broadening becomes noticeable are remarkably independent of the size of the chelate ring or the nature of the substituents, being similar for all of the complexes examined. In the glycol–water and DMSO–water mixtures the broadening at $-35°$, apart from that associated directly with increased viscosity of the solution, probably occurs because N–H protons interact strongly by H bonding with the solvent molecules. As the solvent becomes more rigid, conformational equilibrations will be slowed down.

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Contribution from the Department of Chemistry,
Purdue University, Lafayette, Indiana 47907

Multidentate Ligand Kinetics. XIV. Formation and Dissociation Kinetics of Rare Earth–Cyclohexylenediaminetetraacetate Complexes

By G. A. Nyssen and Dale W. Margerum[1]

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The rate of transfer of *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate (CyDTA) from rare earth ions to copper(II) is dependent on hydrogen ion concentration and independent of copper concentration. The acid dissociation rate constants, k_H^{MCy} (25°, 0.1 μ), vary from the value of 129 M^{-1} sec^{-1} for La(CyDTA)$^-$ to a value of 0.017 M^{-1} sec^{-1} for Lu(CyDTA)$^-$, decreasing in a regular fashion with decreasing ionic radii. All the rare earth 3+ ions (including Y^{3+}) follow this behavior but Sc^{3+} does not. The value for k_H^{ScCy} is 0.019 M^{-1} sec^{-1} which is several orders of magnitude larger than expected from comparison of ionic radii or of stability constants. In direct formation reactions the Sc^{3+} and CyDTA reaction is too fast to measure by stopped-flow methods at pH 4.2. On the other hand La^{3+} reacts at a measurable rate, rapidly forming a weak complex with H(CyDTA)$^{3-}$ followed by a slower first-order reaction in which La^{3+} is incorporated into the coordination cage of the ligand and displaces the proton. With the exception of Sc^{3+} all the ions are much slower in their formation rate constants than expected from their water exchange constants or their reaction with murexide.

Introduction

The rates of formation of complexes of many metal ions (M) with ligands (L) follow the general expression in eq 1 where K_{os} is the outer-sphere association constant and k^{M-H_2O} is the characteristic water exchange constant for the metal ion.[2,3] In the case of multidentate ligands eq 1 often is valid because the first water-substitution step is rate determining. However, the structure of the multidentate ligand can greatly alter the rate from that predicted if several coordination steps must occur simultaneously as is the case in some macrocyclic structures.[4] The reactions of CyDTA (*trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate) with divalent metal ions have been shown[5] to fall into two groups. One group including Co(II), Ni(II),

$$\text{rate} = K_{os}k^{M-H_2O}[M][L] \qquad (1)$$

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