

to be formed at approximately the same rate. These factors, however, are under further investigation.

The resulting tripropenylgallium compounds undergo slow isomerization reactions at room temperature. This precludes the possibility that the isomerization proceeds by the same path as exchange of propenyl groups because it has been shown that this exchange is rapid for trivinylgallium and can be shown to be rapid for tri-*trans*-propenylgallium in the same way. It should be pointed out that a factor which complicates this picture is that upon formation of the TMA adducts of the tripropenylgallium derivatives, the rate of isomerization is greatly reduced since the resulting ad-

ducts can be distilled at 40–80° without isomerization and, in fact, can stand for some time without noticeable change in this form. Thus, it would appear that the bridge bond participates in some way in the isomerization reaction. Both this phenomenon and the "rapid exchange" of the bridge and terminal vinyl groups are under investigation in this laboratory at the present time.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA]

The Proton Magnetic Resonance Spectra and Structures of Ethylenediaminetetraacetic Acid, Methyliminodiacetic Acid, and Nitrilotriacetic Acid Chelates of Molybdenum(VI)¹

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The molybdenum(VI) chelates of ethylenediaminetetraacetic acid (EDTA), methyliminodiacetic acid (MIDA), and nitrilotriacetic acid (NTA) have been studied in aqueous solution as a function of pH (12 to 3) in varying metal-ligand ratios using proton magnetic resonance at 56.4 and 100 Mc. The combining ratios for Mo(VI)-ligand are 1:1 for NTA and MIDA, and 2:1 for EDTA. In the low pH region the methylene protons of the MIDA and EDTA chelates exhibit AB-type splitting which indicates that these protons are nonequivalent. The structures of the chelate molecules are established by interpretation of the spectra. The spectra also indicate that there is nonlabile bonding between Mo(VI) and the carboxylate groups in these chelates.

In a recent study of various aqueous metal-ethylenediaminetetraacetic acid (EDTA) chelate systems using p.m.r.,² the spectrum for the molybdenum(VI)-chelate appeared more complex than the simple two-resonance spectra obtained for the other metal ions. Previous work has shown that the combining ratio of molybdenum(VI) EDTA is 2:1,³ in contrast to the combining ratio of 1:1 exhibited by most of the other chelates of EDTA.

To help elucidate the [Mo(VI)]₂-EDTA n.m.r. spectrum two model chelating agents, methyliminodiacetic acid (MIDA) and nitrilotriacetic acid (NTA), have been studied as well as their molybdenum(VI) chelates. By varying the metal-ligand ratio and the solution pH, the stoichiometry and the ranges of stability can be determined for these chelates.

Experimental

The p.m.r. spectra were recorded at room temperature using a Varian DP-60 high resolution spectrometer, equipped with a 56.4 Mc. oscillator. Chemical shifts were measured in p.p.m. from an external reference of benzene using the conventional side-band technique. No corrections were made for bulk susceptibility. Sample solutions were prepared determinately and normally had a ligand concentration of 0.5 M. The ethylenediaminetetraacetic acid (reagent grade) was obtained from J. T. Baker and Co., the nitrilotriacetic acid was obtained from Matheson, Coleman and Bell, and the methyliminodiacetic acid was obtained from the Aldrich Chemical Co. Molybdic acid (anhydride, reagent grade) was supplied by Baker and Adamson and was used without further purification.

pH measurements were made with a line-operated Leeds and Northrup pH meter employing high range glass electrodes. The pH of a chelate solution was raised initially to some high value with NaOH or KOH and then lowered with HNO₃; n.m.r. samples were taken as the pH decreased.

The 100-Mc. p.m.r. spectra were recorded by Varian Associates, Palo Alto, California.

(1) This work was supported by the United States Atomic Energy Commission under Contract No. AT(11-1)-34, Project No. 45, and by the National Science Foundation with a predoctoral Fellowship to R. J. K.

(2) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963).

(3) R. L. Pecsok and D. T. Sawyer, *ibid.*, **78**, 5496 (1956).

Results

In a previous paper² the changes in chemical shift as a function of pH have been shown for ethylenediaminetetraacetic acid and methyliminodiacetic acid; the positions of protonation of these ligands also have been deduced. A similar study for nitrilotriacetic acid is illustrated in Fig. 1. The first break of the δ vs. pH curve at high pH corresponds to the protonation of the N atom, and the break at lower pH represents the successive protonations of the carboxylate groups.

The n.m.r. resonances obtained for the molybdenum(VI) chelates of EDTA and of MIDA above pH 8, and of NTA above pH 9, are pH dependent and correspond to the spectra for the "free" ligand (that is, for the ligand associated with K⁺ or Na⁺ according to whether KOH or NaOH has been used to raise the pH). Below these threshold pH values the free ligand resonances diminish in intensity and new resonances appear at lower fields. These low-field resonances are independent of pH to the lowest values studied (approximately pH 3). By varying the ratio of metal to ligand and observing the two sets of resonances below the threshold pH values given above, some indication of the stoichiometry of the chelates can be found. Thus, when excess ligand is present a resonance due to the free ligand is observed. However, when the stoichiometric metal-ligand ratio is reached this resonance disappears. Thus, it has been established there are two molybdenum(VI) ions to one ligand for EDTA and one molybdenum ion to one ligand for NTA and MIDA. Henceforth, the results discussed are for solutions containing stoichiometric ratios of molybdenum(VI) and ligand.

The spectrum obtained for Mo(VI)-NTA (Fig. 2) consists of only a single sharp resonance for the methylenic protons. The spectra obtained for Mo(VI)-MIDA (Fig. 3A) and Mo(VI)-EDTA (Fig. 4A) consist of one resonance which can be assigned to the methyl protons or the ethylenic protons, respectively, and a

TABLE I
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR MOLYBDENUM(VI) EDTA, MIDA, AND NTA CHELATES

| Chelate of Mo(VI) | Combining ratio (metal:ligand) | Chemical shifts (p.p.m. from benzene) | | AB quartet ^a | | Ratio of inner to outer resonance intensities | |
|-------------------|--------------------------------|---------------------------------------|--------------------------------------|-------------------------|--------------|---|-------|
| | | Center of quartet | Ethylenic or CH ₂ protons | $\Delta\nu$, c.p.s. | J , c.p.s. | Calcd. | Found |
| EDTA | 2:1 | 2.76 (56.4 Mc.) | 2.60 | 16.5 | 16.7 | 5.9 | 5.2 |
| | | 2.80 (100 Mc.) | 2.64 | 32.2 | 16.7 | 2.7 | 2.8 |
| MIDA | 1:1 | 2.89 (56.4 Mc.) | 3.40 | 13.2 | 16.7 | 8.2 | 6.0 |
| | | 2.86 (100 Mc.) | 3.40 | 35.8 | 16.7 | 3.6 | 3.1 |
| NTA | 1:1 | 2.50 (56.4 Mc.) | (Single resonance, no quartet) | | | | |

^a K. B. Wibery and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 3.

multiplet which we have interpreted as an AB-type splitting of the methylenic protons adjacent to the carboxylate groups. Figures 3B and 4B show the 100-Mc. proton spectra of the MIDA and EDTA chelates as well as the assignments for the different types of protons. The ratios of the integrated intensities of the outer and inner lines of the multiplets agree well with the theoretical values as shown by Table I. The chemical shifts for the molybdenum(VI) chelates also are tabulated in Table I.

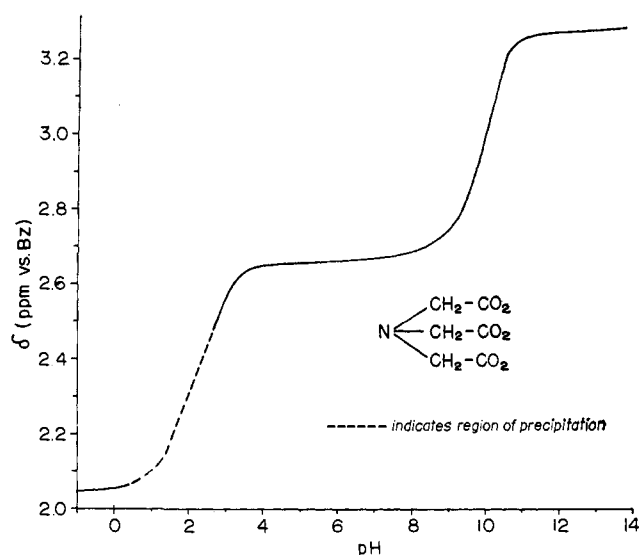


Fig. 1.—NTA as f(pH). KOH used to adjust pH.

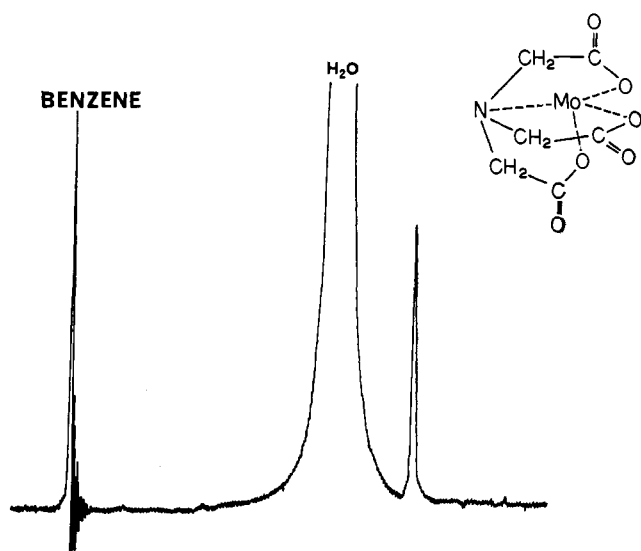


Fig. 2.—Spectra of Mo(VI)-NTA at 56.4 Mc.

The ethylenic proton resonance for [Mo(VI)]₂EDTA, as shown in Fig. 4, occurs at a lower field than the methylenic protons and is in contrast to all the other metal-EDTA systems which have been investigated.²

Conclusions

By analogy with the other strong metal-EDTA systems which previously have been investigated (*i.e.*, an independence of δ on pH),² the Mo(VI) chelates are concluded to be stable below the threshold pH values listed for each of the three ligands (pH 8 or 9); only the free ligands exist above these values. A possible interpretation of this phenomenon is that at high pH values the principal Mo(VI) species in solution is MO_4^{2-} which cannot coordinate with the ligands.

The appearance of a separate set of resonances for the uncomplexed ligand when it is in excess provides evidence that the three chelating agents all form stable and inert complexes with molybdenum(VI). The ligand concentration studies also provide evidence that the metal-ligand combining ratio is 1:1 for MIDA and NTA, and 2:1 for EDTA.

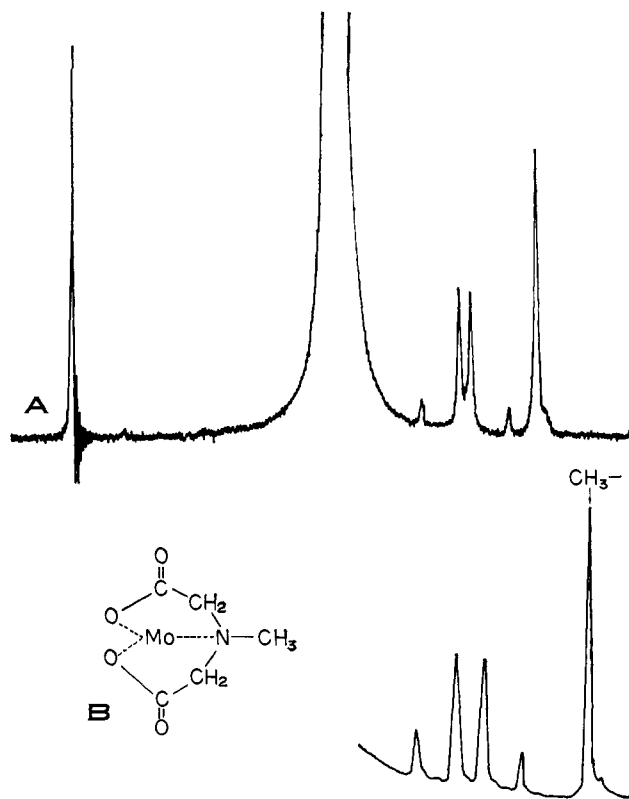


Fig. 3.—A: Spectra of Mo(VI)-MIDA at 56.4 Mc. B: Spectra of Mo(VI)-MIDA at 100 Mc.

Previous work³ on Mo(VI)-EDTA has suggested that the structure of the chelate in aqueous solution is that given in Fig. 4A. The n.m.r. results are consistent with this structure. For Mo(VI)-NTA and Mo(VI)-MIDA the structures depicted in Fig. 2 and 3A, respectively, are postulated. Additional molybdenum-oxygen bonds undoubtedly exist in these chelate molecules, but, for simplicity, are not shown.

For Mo(VI)-MIDA there exists the possibility of *cis* and *trans* isomers. However, the simplicity of the

n.m.r. spectrum suggests the presence of only one isomer under our experimental conditions. Unfortunately, the correct stereochemistry cannot be ascertained. For Mo(VI)-EDTA, in addition to the possibility of *cis* and *trans* carboxylate bonding at each molybdenum atom, the two molybdenums also can be *cis* and *trans* relative to one another along the Mo-N-CH₂-CH₂-N-Mo linkage. Reference to molecular models (Fisher-Taylor-Hirschfelder type) indicates that the conversion between the *cis* and *trans* configurations is highly hindered due to steric factors. Since the four ethylenic protons are equivalent only in the *trans* configuration and only a single sharp resonance is observed for these hydrogens, it is possible to conclude that the isomer under study is that in which the two molybdenums are *trans* with respect to one another. The chemical shifts of the methylenic hydrogens and the $|J|$ value between each nonequivalent pair of protons are nearly equal for both the EDTA and MIDA chelates, indicating that the bonding at the molybdenum atoms must be the same in both cases. The simplicity of the methylene multiplet also indicates that the carboxylate groups are bonded to the molybdenum atoms at both ends of the chelates either both *cis* or both *trans*.

Only one isomer is possible for Mo(VI)-NTA with the structure depicted in Fig. 2. Here because of a threefold axis of symmetry through the nitrogen and molybdenum atoms of the chelate, all six methylenic protons become equivalent. This is in accord with the n.m.r. data.

The carboxylate groups are concluded to be coordinated rigidly to the metal ion in these chelates. In both the EDTA and MIDA chelates this strong carboxylate bonding would result in pairs of nonequivalent methylenic protons, as observed. If the carboxylate bonds were weak and ligands were rapidly coordinating with and dissociating from the metal ion, the spin multiplet for the methylene protons would collapse into a single averaged resonance, as was observed for all the other EDTA chelates investigated thus far.² Although a single resonance is indeed observed for Mo(VI)-NTA, it seems inconceivable that

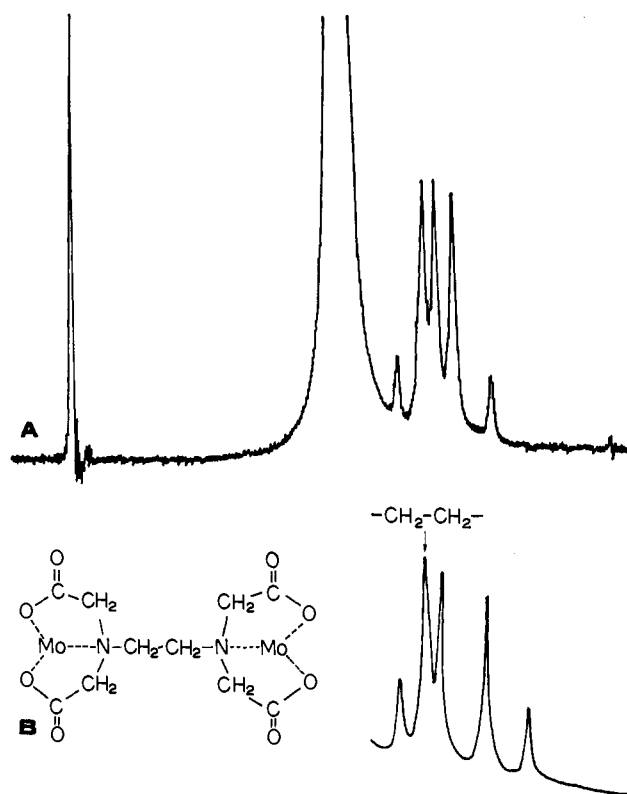


Fig. 4.—A: Spectra of [Mo(VI)]₂-EDTA at 56.4 Mc. B: Spectra of [Mo(VI)]₂-EDTA at 100 Mc.

the nature of the coordination should be different for this ligand.

Finally, it is interesting to note that in Mo(VI)-EDTA, the resonance for the ethylenic protons occurs at a lower field than the center of the multiplet for the methylene protons. This is in contrast to all the other EDTA chelates investigated up to now.² This result can be understood in terms of deshielding effects arising from the close proximity of the oxygen atoms of the Mo=O bonds to the ethylenic protons.

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Studies on Nickel(II) Complexes. V.¹ A Nuclear Resonance Study of Conformational Equilibria

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Complexes of the general type bis-(R-N-salicylaldimine)-Ni(II) in which R is a *sec*-alkyl group have previously been shown to exist in a planar \rightleftharpoons tetrahedral equilibrium in solutions of noncoordinating solvents at and above room temperature.¹ These complexes have now been thoroughly studied by means of proton magnetic resonance and are found to exhibit isotropic proton hyperfine contact shifts. In this respect they are similar to bis-(N,N-disubstituted aminotroponimine)-Ni(II) complexes extensively studied by others.¹⁰ Two sorts of complexes have been examined—those which contain either optically inactive or optically active R groups. For the optically inactive species spin densities on the ligand systems have been evaluated from measurement of contact shifts and magnetic moments. For both the optically inactive and active species analysis of the temperature dependence of the contact shifts has yielded values of ΔF , ΔH , and ΔS for the solution equilibria. Complexes containing optically active groups consist of diastereoisomeric mixtures when prepared from racemic amines. Each diastereoisomer is shown to possess a separate set of contact shifts. The relation of each such set to a given diastereoisomer is proved and it is shown that the thermodynamic parameters for each isomer can be separately determined. The detection of molecular association in solution is demonstrated from contact shift measurements. Procedures for extensive optical resolution ($\geq 95\%$) of two *sec*-alkylamines are reported.

Introduction

As a result of investigations of the past several years, there has now emerged a reasonably clear picture of the

(1) Part IV: R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963).

relation between the magnetic and spectral properties of formally four-coordinate nickel(II) complexes and the immediate coordination environment of the metal ion in these complexes when in solution. Of prime interest have been those complexes which, in solutions of es-