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# Determination of Water Associated with Some Iron Acetylacetonates and Nickel Glyoximes Extracted into $CHCl_3$

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## Summary

Utilizing the Karl Fischer titration technique for the quantitative determination of water, the number of water molecules associated with a molecule of chelate when extracted from water into chloroform was determined for five chelates in the acetylacetone and dimethylglyoxime types. In this investigation no increase in the number of associated water molecules was observed as the bulkiness of the ligand was increased by the substitution of electron-withdrawing groups for methyl groups on the ligand, nor was any increase noted when the metal ion in the chelate was less sterically hindered to the approach of water molecules than in the phenanthroline chelates. The fact that the chelate contains hydrogen-bonded sites does not appear to affect the number of water molecules associated with the chelates investigated here.

It was the purpose of this investigation to further extend the limited knowledge now available concerning the water associated with the extraction of metal chelates. Before a true understanding regarding the nature of solvent extraction and adduct formation can be realized, more information regarding the nature of the extracted species must be available. The number of molecules of water associated with some iron acetylacetonates and nickel glyoximes when extracted into chloroform were to be determined utilizing the Karl Fischer titration technique developed by Meloan and

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Brandt (*10*) and later refined by Gere and Meloan (*8*,*9*). The investigation of associated water with these chelates will provide basic information about two more classes of chelates with regard to their behavior toward adduct formation with water during solvent extraction.

It was desired to investigate a series of acetylacetone chelates, as the previous work was done where the two atoms of the chelate which bond to the metal ion were nitrogen–nitrogen (*2*,*7*,*9*) and nitrogen–oxygen (*8*) but no work where the two atoms were oxygen–oxygen. Other reasons for choosing the acetylacetone chelates include the facts that the effect of subsequent substitution of phenyl groups for methyl groups could be examined, the chemistry of the iron acetylacetonates has been extensively studied (*1*,*5*,*12*), and they have very favorable distribution coefficients for extraction from aqueous solutions (*13*). It seems quite likely that since the structure of the phenanthroline and acetylacetone chelates of iron are similar in many respects that their behavior toward associating with water during solvent extraction might be similar.

An examination of a square-planar complex was deemed worthwhile, for until now there has been no report of an investigation for associated water involving square-planar complexes. A square-planar chelate in solution is nickel dimethylglyoximate, whose chemistry has been well worked out (*4*). If there is water associated with these square-planar chelates, it can attach to the metal ion from above and below the plane of the glyoximes, or since the chelate is hydrogen bonded, this might present another site for water association to the chelate. It was for these reasons that an examination of the square-planar nickel chelates for associated water was performed.

## EXPERIMENTAL

### Chemicals

**2,4-Pentanediene Solution.** Eastman White Label 2,4-pentanediene (acetylacetone) was purified to remove any acetic acid by shaking the liquid with one-tenth its volume of dilute (1:10) ammonia followed by two successive tenth-volume portions of distilled water. The acetylacetone was dried over anhydrous $Na_2SO_4$. Following a water–acetylacetone azeotrope forerun, the pure compound distills. The portion boiling from 135 to 136°C was collected.

It is stable and can be stored almost indefinitely (*11*).

All other chemicals were reagent grade and were used as received.

### Apparatus

**Aquameter.** A Beckman KF-3 Aquameter incorporating dead-stop end-point detection was used for all automatic titrations of water. This has been previously described by Gere (*6,8*).

### Procedure

The procedure utilized in determining the number of molecules of water associated with the particular chelate by the Karl Fischer titration technique was essentially that employed by Gere (*7*) and Burchett (*2*), with suitable modifications where necessary.

The slope and intercept were calculated by the method of least squares described in detail by Gere (*6*).

## RESULTS AND DISCUSSION

In Fig. 1 are shown the ligands which were used in this investigation.

The acetylacetonate chelates investigated in this study can be considered as a series where substitution occurs at the carbonyl group. All three of the chelates studied are octahedral with the acetylacetone acting as a monobasic bidentate chelating reagent. The ring thus formed upon chelation has a partial aromatic character, and for that reason it was thought that its behavior might be similar to that of the phenanthroline chelates investigated previously in this laboratory. These chelates contain pockets in much the same manner as the phenanthrolines and do not offer as much steric hindrance to the approach of water molecules as does the phenanthroline chelates. Gere (*6*) showed that substituting phenyl groups on the phenanthroline chelate of iron greatly increased the amount of water which was associated with this chelate when extracted into organic solvents. This same effect was investigated in the ferric acetylacetonate series discussed here.

All the data of this investigation are of the same general form as that shown in Ref. *6* and for this reason only the results of the least-squares calculations are shown in Table 1.

In looking at the overall results obtained with the series of acetylacetone chelates of iron investigated in this study, it can be stated

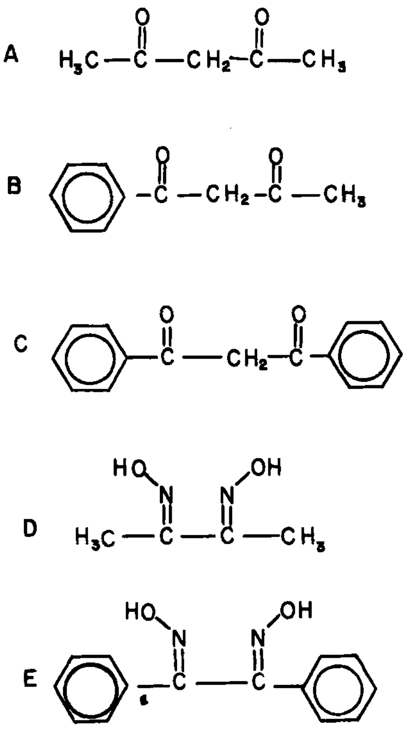

**FIG. 1.** Structure of ligands used. (A) 2,4-Pentanedione; (B) 1-phenyl-1,3-butanedione; (C) 1,3-diphenyl-1,3-propanedione; (D) dimethylglyoxime; (E) diphenylglyoxime.

**TABLE 1**

Results of Least-Squares Determination of the Number of $H_2O$ Molecules Present

| Chelate | $H_2O$ associated | Blank | Net |
|---|---|---|---|
| Tris(2,4-pentanedionate)-iron(III) | 0.2 ± 0.2 | — | 0 |
| Tris(1-phenyl-1,3-butanedionate)iron(III) | 4.6 ± 0.7 | 5.1 ± 0.4 | 0 |
| Tris(1,3-diphenyl-1,3-propane dionate)iron(III) | 4.8 ± 0.2 | 5.5 ± 0.7 | 0 |
| Bis(dimethylglyoximate)-nickel(III) | 3.0 ± 1.1 | 3.0 ± 0.5 | 0 |
| Bis(diphenylglyoximate)-nickel(II) | 18.1 ± 1.5 | 18.1 ± 1.5 | 0 |

that within experimental error there are no molecules of water associated with any of these chelates when they are extracted into $CHCl_3$. The increase in the number of associated water molecules within a given series of chelates attributed to the presence of electron-withdrawing phenyl groups observed by Gere (*7*) does not seem to be a general phenomena, as this present investigation of ferric acetylacetonates clearly points out.

On the basis of these Karl Fischer titrations, we cannot definitely rule out the possibility that water may form an adduct with the ferric acetylacetonates, but if one does form, it is replaced by the chloroform solvent molecule which may be a more stable adduct. Steinbach and Burna (*14*) and Clark et al. (*3*) have studied the halomethane solvates of ferric acetylacetonate and found that chloroform forms a 2:1 adduct having a bonding energy of 4.9 kcal. This would indicate that if water does form an adduct with these acetylacetonates, then upon extraction into chloroform the $H_2O$ molecules are replaced by solvent molecules. This study does not entirely rule out the possibility that a $H_2O$ adduct may form in the aqueous phase but certainly indicates that after extraction into chloroform that a water adduct is not present.

The investigation of the two square-planar complexes of nickel show that apparently $H_2O$ will not associate with the already extensively intramolecularly hydrogen-bonded portion of the chelates. Here again, as in the previously discussed acetylacetone series, the presence of phenyl groups did not increase the number of associated $H_2O$ molecules, as Gere and Meloan (*8*) observed in the phenanthroline series.

## CONCLUSIONS

Utilizing the Karl Fischer titration technique for the quantitative determination of water, the number of water molecules associated with a molecule of chelate when extracted from water into chloroform was determined for five chelates in the acetylacetone and dimethylglyoxime types. Least-squares analysis of the data obtained showed that the chelates tris(2,4-pentanedionate)iron(III), tris(1-phenyl-1,3-butanedionate)iron(III), tris(1,3-diphenyl-1,3-propanedionate)iron(III), and bis(diphenylglyoximate)nickel(II) have 0.2 ± 0.2, $-0.5 \pm 0.8$, $-0.7 \pm 0.7$, $0.0 \pm 1.2$, and $0.5 \pm 2.1$ molecules of water associated with a molecule of each chelate, respectively. In this investigation no increase in the number of associated water molecules was observed as the bulkiness of the ligand was increased by the substitution of electron-withdrawing groups for methyl groups on the ligand, nor was any increase noted when the metal ion in the chelate was less sterically hindered to the approach of water molecules than in the phenanthroline chelates. The fact that the chelate contains hydrogen-bonded sites does not appear to affect the number of water molecules associated with the chelates investigated here.

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