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Water Adduct Formation in Extracted Chelates

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Summary

Water adducts of 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, tris(4,7-diphenyl-1,10-phenanthroline) Fe(II) perchlorate, tris(4,7-diphenyl-1,10-phenanthroline) Ru(II) chloride, tris(1,10-phenanthroline) Fe(II) perchlorate, and bis(2,9-dimethyl-1,10-phenanthroline) Cu(I) perchlorate had 5.1 ± 0.9, 0 ± 1.3, 6.8 ± 0.6, 5.6 ± 1.5, 4.8 ± 0.7, 6.3 ± 0.6, and 6.5 ± 1.0 molecules of H_2O, respectively, associated with them when they were extracted into nitromethane. All deviations are at the 95% C.I.

The purpose of this project was to investigate adduct formation resulting in solvent extraction. The adduct of interest was water. It has been shown by Meloan and Brandt (7) and Gere and Meloan (2,3) that water is associated with certain chelates when these compounds undergo extraction.

In this investigation the number of associated water molecules was determined by the Karl Fischer technique utilized by Meloan and Brandt (7) and later refined by Gere and Meloan (2,3).

The chelates used in this investigation were tris(4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate, tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) chloride, tris(1,10-phenanthroline) iron(II) perchlorate, and bis(2,9-dimethyl-1,10-phenanthroline) copper(I) perchlorate. The first three chelates have d^2sp^3 bonding which gives an octahedral structure. The last chelate has sp^3-type bonding which gives a tetrahedral structure. The abbreviations

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Fe(bath)$_3^{2+}$, Ru(bath)$_3^{2+}$, Fe(phen)$_3^{2+}$, and Cu(neo)$_2^{+}$ will be used, respectively, to designate the chelates.

EXPERIMENTAL

The experimental technique is described in detail in Refs. *2*, *3*, *6*, and *7*.

Procedure

Karl Fischer Titration Method. The method used was that employed by Gere and Meloan (*2*,*3*); however, the blank was determined differently.

The blank determination in this investigation consisted of preparing ligand concentrations corresponding to those used in the chelate preparation. These ligand solutions were treated as above to get the number of water molecules associated with three ligand molecules [two in the case of Cu(neo)$_2^{+}$], three being the number of ligand molecules in the chelate. The difference between the value for the chelate and the ligand is the amount of additional water that becomes associated upon chelation.

Extraction of Chelates. Three of the four chelates were prepared and extracted as in Refs. *2*, *3*, and *7*.

Tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) chloride required special attention and was prepared according to Vita and Trivisonno (*10*). This consisted of combining a given amount of 0.01 *M* ruthenium trichloride, 1 ml of 10% hydroxylamine hydrochloride, 1 ml of 10% sodium acetate, and an appropriate amount of 0.01 *M* 4,7-diphenyl-1,10-phenanthroline in ethanol. This solution was diluted with deionized water to 40 ml and heated for 2 hr in a boiling-water bath. The resulting chelate was extracted with 30 ml of nitromethane and treated as described above.

The blanks were treated the same as the chelates, except no metal ion was present.

RESULTS AND DISCUSSION

Determination of Associated Water

A typical set of data and the associated least-squares treatment is given in Table 1. These results are for the extraction and titration of Fe(bath)$_3^{2+}$. In this table the chelate concentration is the x variable

TABLE 1

Karl Fischer Titration Results and Least-Squares Treatment for Fe(bath)$_3^{2+}$ Extracted from H_2O into CH_3NO_2

x, [Fe(bath)$_3^{2+}$] × 10^5/5 ml CH_3NO_2	y, [H_2O] × 10^5/5 ml CH_3NO_2	xy	x^2
0	654.56	0	0
0	657.20	0	0
0	655.15	0	0
0	649.56	0	0
1.0	666.03	666.03	1.0
1.0	663.53	663.53	1.0
1.0	665.59	665.59	1.0
1.0	663.53	663.53	1.0
3.0	680.44	2,041.32	9.0
3.0	678.83	2,036.49	9.0
3.0	676.32	2,028.99	9.0
3.0	676.62	2,029.86	9.0
5.0	687.65	3,438.25	25.0
5.0	683.98	3,419.90	25.0
5.0	685.89	3,429.45	25.0
5.0	680.44	3,402.20	25.0
36.0	10,725.33	24,485.14	140.0

$$\text{Slope} = \frac{n[xy] - [x][y]}{n[x^2] - [x]^2} = \frac{(16.00)(24{,}485.14) - (36.00)(36.00)(10{,}725.33)}{(16.00)(140.00) - (36.00)^2} = 5.98$$

$$\text{Int.} = \frac{[x^2][y] - [x][xy]}{n[x^2] - [x]^2} = \frac{(140.00)(10{,}725.33) - (36.00)(24{,}485.14)}{(16.00)(140.00) - (36.00)^2} = 656.86$$

and the water concentration is represented by y. The calculated slope gives the number of water molecules associated with the chelate or ligand and the intercept gives the solubility of water in 5 ml of nitromethane expressed in moles times 10^5.

The number of associated water molecules was determined five times for most chelates and ligands. At least three determinations were necessary statistically. Obviously more determinations would be desirable, but it was decided that this was not practical because of the expense of the reagents and because this technique probably is not much better than the ±0.5 molecule of water which was obtained in some cases.

Also, only one value for a given chelate could be obtained in 1 day; therefore 3 to 5 days elapsed between the first and last result.

This length of time would be sufficient to allow for any deviations in variables such as pipeting, weighing, and temperature of the water bath. Thus it is felt that the results obtained were reliable and that additional runs would not reduce the deviation significantly.

The data for each set of titrations are calculated the same as that given in Table 1. Therefore only the slopes are tabulated in Tables 2–5.

At the bottom of each table is given the number of additional water molecules which become associated upon chelation, i.e., the difference between the slope of the chelate and the slope of the ligand.

The ligand should be considered particularly in this case because it has been shown that certain phenanthrolines have water associated with them and that this water is hydrogen bonded to the nitrogens (*4*,*9*), which are the electron donors in chelate formation.

After observing the results, the importance of the ligand is further realized. Consider the case of tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate and tris (1,10-phenanthroline) iron(II) perchlorate (*1*). Upon comparing these chelates, one notices that the method of preparation, the metal ion, the anion, and the number of associated water molecules are the same (within the deviations):

TABLE 2

Results of Karl Fischer Titrations for the Ligands and Chelates Used in this Investigation

Fe(bath)$_3^{2+}$ slopes			Bath slopes		
Value	Dev.	Dev.^{2}	Value	Dev.	Dev.^{2}
5.73	0.11	0.01	−1.10	1.10	1.21
5.21	0.41	0.17	0.69	0.69	0.48
5.98	0.36	0.13	−0.72	0.72	0.52
3.95	1.67	2.79	1.42	1.42	2.02
7.25	1.63	2.66	−0.56	0.56	0.31

Avg. = 5.6
Avg. dev. = ±0.8
Std. dev. = −1.0
C.I. (95%) = ±1.5

Avg. = 0
Avg. dev. = ±0.9
Std. dev. = +0.9
C.I. (95%) = ±1.3

Difference between chelate and ligand: 5.6 ± 2

TABLE 3

Results of Karl Fischer Titrations for the Ligands and Chelates Used in this Investigation

$Fe(phen)_3^{2+}$ slopes			Phen slopes		
Value	Dev.	$Dev.^2$	Value	Dev.	$Dev.^2$
6.71	0.40	0.16	4.20	0.87	0.76
6.60	0.29	0.08	5.03	0.04	0.00
6.31	0.00	0.00	5.89	0.82	0.67
5.57	0.74	0.55	5.16	0.09	0.01
6.36	0.06	0.00			

Avg. = 6.3	Avg. = 5.1
Avg. dev. = ±0.3	Avg. = ±0.5
Std. dev. = ±0.4	Std. dev. = ±0.7
C.I. (95%) = ±0.6	C.I. (95%) = ±0.9

Difference between chelate and ligand: 1.2 ± 0.8

TABLE 4

Results of Karl Fischer Titrations for the Ligands and Chelates Used in this Investigation

$Cu(neo)_2^+$ slopes			Neo slopes		
Value	Dev.	$Dev.^2$	Value	Dev.	$Dev.^2$
6.13	0.32	0.10	7.40	0.59	0.35
6.45	0.00	0.00	7.30	0.49	0.24
6.77	0.32	0.10	6.74	0.07	0.00
5.26	1.19	1.42	6.17	.64	0.41
7.64	1.19	1.42	6.42	0.39	0.15

Avg. = 6.5	Avg. = 6.8
Avg. dev. = 0.7	Avg. dev. = ±0.4
Std. dev. = 0.9	Std. dev. = ±0.5
C.I. (95%) = ±1.0	C.I. (95%) = ±0.6

Difference between chelate and ligand: 0 ± 1

TABLE 5

Results of Karl Fischer Titrations for the Ligands and Chelates Used in this Investigation

Ru(bath)$_3^{2+}$ slopes			Bath slopes		
Value	Dev.	Dev.^{2}	Value	Dev.	Dev.^{2}
4.91	0.07	0.00	−1.10	1.10	1.21
4.99	0.15	0.02	0.69	0.69	0.48
5.42	0.42	0.18	−0.72	0.72	0.52
4.03	0.81	0.66	1.42	1.42	2.02
			−0.56	0.56	0.31
Avg. = 4.8			Avg. = 0		
Avg. dev. = ±0.4			Avg. dev. = ±1		
Std. dev. = ±0.5			Std. dev. = ±1		
C.I. (95%) = ±0.7			C.I. (95%) = ±1.3		

Difference between chelate and ligand: 4.8 ± 1.5

5.6 ± 0.8 for Fe(bath)$_3^{2+}$ and 6.3 ± 0.3 for Fe(phen)$_3^{2+}$. However, one major factor is different and this is the ligand. Bathophenanthroline has only 0 ± 1 associated water molecule, while 1,10-phenanthroline has 5.0 ± 0.4. Subtracting these values from the results for the chelates, one gets 6 ± 1 and 1 ± 0.5 additional water molecules upon chelating for Fe(bath)$_3^{2+}$ and Fe(phen)$_3^{2+}$, respectively.

Whether or not the water with the ligand becomes involved with the chelate cannot be determined from the techniques used in this investigation. However, it appears that this is a likely possibility because of its proximity to the site of chelation. One way of determining this would be to use deuterated water to prepare 1,10-phenanthroline monodeuterate, which could then be used to prepare Fe(phen)$_3^{2+}$. Then one could observe the OH stretching frequency of the water associated with the chelate to see if it has shifted to a lower frequency, which would indicate that D_2O was bonded to the chelate.

Using the observation of Jensen et al. (5), one notices an interesting phenomenon when the titration results are reviewed. These authors state that "the rigid, planar structure of phenanthroline lends certain geometrical characteristics to the complex." They say that in octahedral complexes the three phenanthroline molecules form perpendicular planes which have pockets between them.

Models show that two water molecules can fit into each pocket for a total of six water molecules. This produces a spherical molecule.

With this in mind one notices that two of the three octahedral chelates, Fe(bath)$_3^{2+}$ and Fe(phen)$_3^{2+}$, have six water molecules associated with them, which tends to verify the above observation. The fact that Ru(bath)$_3^{2+}$ has only 4.8 ± 0.4 molecules could be due to its additional electrons which would tend to repel the available electrons on the oxygen of water, thus reducing the amount of water that would set in these pockets.

The value of 6.5 ± 0.7 for Cu(neo)$_2^+$ appears to be high due to the blocking action of the 2 and 9 methyl groups. However, this is a tetrahedral chelate and the structure is such that there is space between the methyl groups themselves and the between the methyl groups and the adjacent phenanthroline molecules, thus leaving enough room for water molecules to set between the phenanthroline planes. Also, the tetrahedral covalent radius of Cu$^+$ (1.35 Å) (*8*) is larger than octahedral covalent radius of Fe^{2+} (0.23) in Fe(phen)$_3^{2+}$; therefore this should give more space for water molecules to fit in the pockets between the phenanthroline planes.

A model of Cu(neo)$_2^+$ shows that water molecules can set in the chelate.

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