THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

PART IV*. CATIONS OF Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn AND Pb

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In the preceding articles of the present series mention was made¹⁻³ of the uncertainty in the literature about the products formed in the reactions of diphenylcarbazide and diphenylcarbazone with cations. The most important problem in the reactions studied proved to be the question whether both carbazone and carbazide⁴ or only carbazone⁵ form metal complexes.

For copper(II) some interesting observations about this problem have been reported. TURKINGTON AND TRACY⁶, using JOB's method⁷, found that two molecules of carbazide react with one copper(II) ion; from transference measurements they concluded that an uncharged complex was formed, which they believed to be derived from carbazide. THARUR AND HALDAR⁸, from the analysis of the precipitated complexes in the reactions of copper(II) acetate and sulphate, concluded that the following products were formed (H₂D = diphenylcarbazone; H₂Di = diphenylcarbazide; HOAc = acetic acid):

> copper sulphate + carbazide: Cu(HDi)₂ copper sulphate + carbazone: Cu(HD)₂ copper acetate -+ carbazide: Cu₃(OAc)₂Di copper acetate -+ carbazone: Cu₃(OAc)₂D

In the last two reactions the complexes seem to contain copper(I) as well as copper(II).

In this article the nature and composition of the products formed with the cations mentioned in the title, are described. In a following article the determination of the equilibrium constants will be described.

EXPERIMENTAL

A detailed description of reagents, solvents and apparatus used can be found in the preceding articles^{2,3}. The following salts were used: manganese(II) nitrate, iron(II) sulphate, iron(III) chloride and nitrate, cobalt(II) perchlorate, nickel(II) perchlorate, copper(II) chloride and bromide, copper(II) perchlorate and sulphate, zinc perchlorate, cadmium perchlorate, tin(II) chloride and nitrate, tin(IV) chloride and nitrate,

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lead(II) nitrate and lead(IV) nitrate. The copper(II) and cadmium perchlorates were prepared by dissolving the oxides in a perchloric acid solution; the lead and tin nitrates by dissolving the "hydroxides" in dilute nitric acid. The other salts were available in p.a. quality.

Experiments involving the ions Cu(I), Sn(II), Fe(II) and Co(II), which were readily oxidizable under the experimental conditions, were performed under nitrogen.

RESULTS

Preliminary experiments

Reactions with diphenylcarbazone. Solutions of the salts mentioned above, in an alcohol-water mixture (20:80, v/v) react immediately with solutions of carbazone in the same solvent to form coloured complexes; only tin(IV) and lead(IV) do not react. The concentrations of both reagent and salts were $10^{-3}M$; for each cation the pH had to be chosen at a special value, in every case lying between 2 and 7.

The complexes form colloidal solutions as is obvious from the Tyndall effect and from the flocculation on heating or on addition of an indifferent electrolyte.

Just as we observed³ in the case of mercury, we found that the copper(I) and (II) complexes are bleached on irradiation of the solutions with ultraviolet and visible light. The decomposition also takes place in the dark, but the rate is slower; in this case the reaction proved to be a first order one (from a plot of log extinction vs. time). In the decomposition of both the copper(I) and copper(II) complexes in the dark and in the light, metallic copper and diphenylcarbodiazone are formed finally; furthermore, a number of non-identified intermediates were observed. With the complexes of the other cations neither bleaching nor decomposition on irradiation or in the dark was observed.

Reactions with diphenylcarbazide. None of the non-oxidizing ions of the salts mentioned in the experimental part, reacts with freshly recrystallized diphenylcarbazide, provided that the solutions of metal salts and carbazide are made oxygen-free by bubbling nitrogen through the solutions. In these experiments the solvent was an alcohol-water mixture (20: 80, v/v), the concentration of the carbazide was $5 \cdot 10^{-3} M$, and that of the cations $10^{-2} M$; the pH was varied between 1 and 8 for each cation.

The oxidizing cations of mercury(I) and (II) do react with carbazide³; Pb(IV) and Sn(IV) do not react under the circumstances described for the non-oxidizing ions.

Concerning the cations of copper(II) and iron(III) the following observations were made.

Copper: Because of their sensitivity to light the copper complexes were handled in the dark.

With carbazide, copper(II) reacts more slowly than with carbazone. A series of experiments was performed, in which 50–150 ml of a solution of copper(II) perchlorate in water $(10^{-3}-10^{-4} M)$ was added to the same volume of an equimolar solution of carbazide in alcohol. After mixing, the pH was adjusted to 4.0 to complete the reaction. After about 30 min to await complete flocculation, the precipitate was filtered and washed with water. With this precipitate the following experiments were performed:

(*t*) The precipitate was decomposed on the filter with 25 ml of 5 N hydrochloric acid; diphenylcarbazone and metallic copper, which were identified as such, remained on the filter. In the filtrate, the following tests gave the results indicated. *p*-Dime-

thylaminobenzylidenerhodanine showed a positive test for copper(I). Rubeanic acid gave a weakly positive test for copper(II) (probably formed by the oxidation of copper (I)). A test for diphenylcarbazide with chromate was negative; in testing for carbazone, on the addition of sodium hydroxide, the red anion was formed.

(2) The total copper content of the precipitate was determined by dissolving it, after drying, in a mixture of 2 ml of concentrated sulphuric and I ml of perchloric acid, followed by a copper(II) titration with 0.01 M EDTA⁹. The results were 29.8% and 30.0% Cu.

(3) In a solution obtained by dissolving the filtered precipitate in 25 ml of 5 N hydrochloric acid, copper(I) was determined after the carbazone formed had been extracted with toluene: iron(III) chloride was added to the copper solution in excess and the iron(II) formed was titrated with 0.01 N ceric sulphate, using ferroin as an indicator. A comparison of the original quantity of copper(II) and diphenylcarbazide with the copper(I) formed showed that $1.5 \cdot 10^{-1}$ mmole Cu²⁺ + $1.5 \cdot 10^{-1}$ mmole carbazide yielded $0.8 \cdot 10^{-1}$ mmole Cu(I) complex.

Job curves for the system copper(II)-diphenylcarbazide in an alcohol-water mixture (50:50, v/v) at pH 4.0 and a total concentration of $9.7 \cdot 10^{-4} M$, show a maximum (Fig. 1) at a Cu²⁺: carbazide ratio of 3:2. Job curves of the system copper(II)-diphenyl-

1.2 1.2 1.0 1.2 1.0 0.8 0.6 0.40 0.50Mole fraction of carbazide

Fig. 1. Job curves for the system copper(II)-diphenylcarbazide. (a) $\lambda = 540 \text{ m}\mu$; (b) $\lambda = 520 \text{ m}\mu$.

carbazone and copper(I)-diphenylcarbazone in the two-phase system water-toluene have maxima (see below) at the ratios Cu^{2+} : carbazone = 1:2 and Cu^+ : carbazone = 1:1.

The observations described above allow the reactions for the copper systems to be formulated as follows:

I $Cu^{+} + H_2Di \longrightarrow$ no reaction II $Cu^{+} + H_2D \iff CuHD + H^+$ III $3Cu^{2+} + 2H_2Di \iff 2CuHD + Cu + 6H^+$ IV $Cu^{2+} + 2H_2D \iff Cu(HD)_2 + 2H^+$

Reaction III would involve a value of 28.5% for the total copper content of the precipitate mentioned in (2), and a value of 10^{-1} mmole for the yield of copper(I)

mentioned in (3). In view of the losses of copper(I) caused by oxidation and by the various manipulations involved, the agreement with the experimental values is fairly good.

Our results do not agree with the conclusions drawn by TURKINGTON AND TRACY⁶. Their experiments, however, were performed at pH 9.0, where hydrolysis of the copper (I) and (II) and oxidation of the carbazide by atmospheric oxygen before complex formation are likely to cause changes in the Job curves. Because the compound formed in reaction III is a copper(I) complex, the impossibility of obtaining a reaction between Cu(II) and carbazone at pH 9.0, as these authors report, does not prove that the compound formed is a carbazide complex.

Iron: Iron(III) reacts with diphenylcarbazide, but more slowly than with carbazone. The formation of a complex is obvious from a change in the absorption spectrum; a shoulder on the extinction curve appears at 500 m μ , characteristic of the carbazone complexes.

The colloidal complex was flocculated, filtered, washed with water and alcohol and then decomposed on the filter with a 4 N perchloric acid solution, which left diphenylcarbazone on the filter. In the perchloric acid solution the followings tests were made. Testing with hexacyanoferrate(III) gave a positive result for iron(II); a positive test for iron(III) was obtained with thiocyanate. In the test for diphenylcarbazone, the red anion was formed with sodium hydroxide; a negative result was obtained on testing for the carbazide with chromate.

The slow reaction and the oxidation by iron(III) of the complex formed made it impossible to obtain quantitative results. However, it is evident that in the reaction of iron(III) with diphenylcarbazide a carbazone complex is formed.

Composition of the complexes

Job curves for the systems M^{n+} -carbazone in the two-phase system, water-toluene, were measured for the metals that react with this reagent. Toluene was chosen as the



Fig. 2. Job curves for the systems M^{n+} -diphenylcarbazone in the two-phase system, water-toluene. Experimental conditions are summarized in Table I.

solvent for the extraction because the more widely used chloroform and carbon tetrachloride often showed adsorption of the complexes on the interface between water and the organic solvent. The shaking time was 2-3 min. The extinction of the toluene layer was measured at three wavelengths with intervals of 10-25 m μ . As the shape of the curves for the three wavelengths did not differ appreciably, only one curve was plotted in Fig. 2 for each system; the Job curves for mercury(I) and (II)³ are also given for comparison purposes.

For the divalent cations the ratio of metal to carbazone at the maximum appeared to be 1:2; for copper(I) it was 1:1, for iron(III) it was 1:3.

The experimental conditions are summarized in Table I; with many systems the presence of a buffer was necessary: Asmus¹⁰ has shown that in this case the maximum is not shifted.

Curve	System	$\lambda(m\mu)$	Total concentration (M)	pН	Medium
I	Mn ²¹ -H ₂ D	520	3.32 * 10**3	7.45	Buffer A*
2	$Ni^2 + H_2D$	500	7.0.10-4	7.43	Buffer B**
3	Zn ² '-H ₂ D	530	8.0+10-4	6.00	Buffer A
4	Hg2 ²⁺ -H2D	500	3.4.10-5	2.0	I M KNOa
5	1,1)2+-1121)	540	5.0.10-4	6.50	Buffer A
6	Fe ²⁺ -H ₂ D	510	5.4.10-4	6.00	Buffer A
7	$Co^2 + -H_2D$	550	2.07 - 10-3	5.30	Buffer A
Š	Cu+-H ₂ D	550	2.9.10-4	3.75	1 M NaCl
9	Cu ²⁺ -H ₂ D	550	7.8.10-5	4.00	D. I. M. NaClO
10	$Hg_2^2 + - H_2D$	500	1.7.10-5	3.00	1 M KNO3
11	Fe ³⁺ -HaD	510	2.41 10-3	1.0	O.T.M.NaClO
12	Cd^{2} - $H_{2}D$	480	8.0+10-4	7.50	Buffer A
13	Hg ²⁺ -H ₂ D	550	3.0.10-4	3.00	Buffer B
14	Hgat-Hall	550	3.7.10-4	0.0	HClO
15	Sn ²⁺ -H ₂ D	530	1.8.10-4	3.00	o.t M NaNO

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EXPERIMENTAL CONDITIONS FOR THE JOB CURVES

* Buffer Λ = acetic acid + sodium acetate; 0.2 M.

** Buffer $B = \text{citric acid} + \text{Na}_2 \Pi PO_4$; 0.2 M.

To check the possible formation of more than one complex for the systems of Fig. 2, solutions of the lowest complex were prepared by completely converting the diphenylcarbazone in 10^{-5} M toluene solution into the complex by equilibrating the solution with an aqueous phase containing M^{n+} in excess at a pH which was selected high enough to guarantee the completeness of the reaction. The completeness of the conversion was checked by measurement of the extinction. In the toluene solutions of the complexes obtained in that way, carbazone was dissolved in excess up to concentrations of 10^{-3} M. After a correction for the extinction of the free carbazone, the extinction of the solutions proved to be constant for all metal complexes with the exception of mercury(I) and (II)³. This means that with the exception mentioned, every cation forms only one complex, the composition of which is given by the Job curves of Fig. 2.

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CONCLUSION

The experiments described show that the metal ions which react with diphenylcarbazone can react with the carbazide only after a preceding oxidation of this reagent, and that diphenylcarbazide itself does not form any metal complexes. The conclusion must be drawn that the carbazide complexes described in the literature really are formed after oxidation of the carbazide, for instance by atmospheric oxygen, which generally has not been excluded by suitable precautions.

In a following publication we intend to describe the determination of the extraction dissociation constants of the carbazone complexes in the system water-toluene.

A detailed description together with possible structures has been published elsewhere¹¹.

SUMMARY

Of the cations mentioned in the title, only Pb(IV) and Sn(IV) do not react with diphenylcarbazone. The compositions of the carbazone complexes were determined by Job's method; the formula proved to be $M(HD)_n$ according to the valence of the cation. Diphenylcarbazide forms metal complexes only after its oxidation to diphenylcarbazone. Oxidation of carbazide by the metal ion itself occurs with copper(II) and iron(III).

RÉSUMÉ

De tous les cations mentionnés dans le titre, seuls Pb(IV) et Sn(IV) ne réagissent pas avec la diphénylcarbazone. La composition des complexes formés a été déterminée par la méthode de Job; on arrive à la formule M(HD),, suivant la valence du cation. La diphénylcarbazide ne peut former des complexes métalliques qu'après oxydation en diphénylcarbazone. L'oxydation de la carbazide par le métal lui-même se produit avec le cuivre(II) et le fer(III).

ZUSAMMENFASSUNG

Von den im Titel erwähnten Kationen reagieren Blei(IV) und Zinn(IV) nicht mit Diphenylearbazon. Für die Zusammensetzung der Diphenylcarbazon-Komplexe wurde nach der Jobschen Methode die Formel M(HD), gefunden. Metallkomplexe werden nur gebildet, nachdem das Diphenylcarbazid zum Diphenylcarbazon oxidiert worden ist. Kupfer(II)- und Eisen(III)-Ionen vermögen Diphenylcarbazid zu oxidieren.

REFERENCES

- ¹ E. VAN DALEN AND S. BALT, Anal. Chim. Acta, 25 (1961) 507.
- ² S. BALT AND E. VAN DALEN, Anal. Chim. Acta, 27 (1962) 188.
- ³ S. BALT AND E. VAN DALEN, Anal. Chim. Acta, 27 (1962) 416.
- 4 F. FEIGL AND A. F. LEDERER, Monatsh. Chem., 45 (1924) 63, 115.
- ⁵ M. P. CAZENEUVE, Compt. Rend., 131 (1900) 346, 1478.
- ⁶ R. W. TURKINGTON AND F. TRACY, Anal. Chem., 30 (1958) 1099.
- 7 P. JOB, Ann. Chim. (Paris), 109 (1928) 113.
 8 S. P. THAKUR AND B. C. HALDAR, Sci. Cult. (Calcutta), 27 (1961) 89.
- 9 G. SCHWARZENBACH, Die komplexometrische Titration, Ferdinand Enke, Stuttgart, 1957.
- ¹⁰ E. ASMUS, Z. Anal. Chem., 183 (1961) 401.
- 11 S. BALT, Dissertation, Amsterdam, 1962.

Anal. Chim. Acta, 29 (1963) 466-471