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Studies on Stabilities of Nickel(II) and Zinc(II) Complexes of Substituted Diphenylcarbazones and Thiocarbazones[†]

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The influence of electron-withdrawing substituents on the formation constants of the complexes of nickel(II) and zinc(II) with substituted diphenylcarbazones and diphenylthiocarbazones has been studied. Change of the environment had a profound influence on the spectra of the ligands containing nitro groups.

Introduction

For many years (*1–4*), the structural interpretation of the properties of metal complexes of diphenylcarbazone (DPC), diphenylthiocarbazone (DPTC), and their various analogues has received considerable attention. In continuation of this work, we have now undertaken a systematic study of the influence of electron-withdrawing substituents on the formation constants of the complexes of nickel(II) and zinc(II) with substituted DPC and DPTC. Formation constants of the complexes were studied both by the Calvin–Bjerrum titration method and a spectrophotometric method. Due to the limited solubility of DPTC and its derivatives, a spectrophotometric method was employed. In contrast, higher solubility of DPC and its derivatives prompted us to use the Calvin–Bjerrum method. The ligands used were the carbazones and thiocarbazones of bis(2-methyl-5-nitrophenyl), bis(4-methyl-2-nitrophenyl), bis(2-methyl-4-nitrophenyl), bis(4-methyl-3-nitrophenyl), and bis(2,6-dimethylphenyl). It was observed that the change of the environment had a profound influence on the spectra of the ligands containing nitro groups.

Experimental Section

***Reagents*.** Carbazones of bis(2,6-dimethylphenyl), bis(2-methyl-5-nitrophenyl), bis(4-methyl-2-nitrophenyl), bis(4-methyl-3-nitrophenyl), and bis(2-methyl-4-nitrophenyl) were prepared by the method of Ghosh and Ray (*5*). The corresponding carbazides needed for the preparation of carbazones were prepared by adding a calculated quantity of 20% phosgene in toluene to the ice-cooled and well-stirred ethanol solution of the respective hydrazines (*6*). A BDH sample of DPC was purified by the method suggested by Krumholz and Krumholz (*7*); the purity of these compounds was assessed by a potentiometric method. DPTC (Fisher Scientific Co.) was purified by the procedure of Cowling and Miller (*8*). Thiocarbazides of bis(2,6-dimethylphenyl), bis(2-methyl-5-nitrophenyl), bis(4-methyl-2-nitrophenyl), and bis(2-methyl-4-nitrophenyl) were prepared by the method described elsewhere (*9*). Thiocarbazides were prepared by refluxing the respective hydrazine and carbon disulfide in 95% ethanol for about 6 h. These thiocarbazides were then converted into thiocarbazones by treatment with alcoholic potash. The crude samples of thiocarbazones were then purified in the same way as those of DPTC. Analar 1,4-dioxan was purified by refluxing it with metallic sodium. All the compounds used for the preparation of buffers were of reagent grade. The metal perchlorates of nickel, zinc, and sodium were obtained from G.F. Smith Chemical Co. All solutions were made with deionized water and freshly distilled dioxan. The metal salt solutions were standardized by EDTA titrations.

Table I. Acid Dissociation Constants of Diphenylthiocarbazone and Formation Constants of Their 1:1 Metal Chelates in 50% (v/v) Aqueous Dioxan

		log K_{f_i}		log K_{pd}[a]	
diarylthiocarbazone	pK_a	Ni(II)	Zn(II)	Ni(II)	Zn(II)
diphenyl	5.90	6.00	6.14	0.10	0.24
bis(2,6-dimethylphenyl)	7.30	7.41	5.99	0.11	−1.31
bis(2-methyl-5-nitrophenyl)	3.15	3.86	3.25	0.71	0.10
bis(4-methyl-2-nitrophenyl)	6.70	5.03	4.33	−1.67	−2.37
bis(2-methyl-4-nitrophenyl)	4.78	5.91	4.61	1.13	−0.17
bis(4-methyl-3-nitrophenyl)	2.75	4.83	4.22	2.08	1.47
bis(*o*-methylphenyl)[b]	6.23	5.90	4.50	−0.33	−1.73
bis(*p*-methylphenyl)[b]	6.40	6.60	6.45	0.20	0.05

[a] $\log K_{pd} = \log K_{f_i} - pK_a$. [b] Reference *1*.

***Apparatus and Method*.** A Toshinwal make pH meter Model CL-43 was used throughout this work. A Specord UV–visible spectrophotometer, Carl-Zeiss Jena was used for optical density measurements. Proton–ligand and metal–ligand stabilities of DPC and substituted DPC–metal compounds were determined by the Calvin–Bjerrum method as modified by Irving and Rossotti (*10*) in 0.1 ionic strength at 25 °C. pK_a values were obtained by intercepts of the linear plots of log $[\bar{n}_A/(1 - \bar{n}_A)]$ vs. pH (where $\bar{n}_A$ is the average number of protons per ligand). Metal–ligand stability constants were obtained from half-integral values of plots of $\bar{n}$ vs. pL.

The acid dissociation constants of DPTC and its various analogues at 0.1 ionic strength in 50% (v/v) aqueous dioxan were calculated by using (*1*)

$$\mathrm{pH} = \mathrm{p}K_a + \log\left[\frac{\epsilon_{HL}T_L - A}{\epsilon_A - \epsilon_L T_L}\right] \qquad (1)$$

The formation constants were calculated from

$$\log K_{f_1} = \mathrm{p}K_a - \log T_M - \mathrm{pH} + \log\frac{(A - \epsilon_{HL}T_L)}{(\epsilon_{ML}T_L - A)} \qquad (2)$$

Here, ϵ_{HL} ϵ_L, and ϵ_{ML} represent the molar absorptivity of neutral, anionic forms of the ligand and 1:1 metal complex, respectively, and T_L and T_M represent the total concentrations of the ligand and metal, respectively. A is the absorbance at a given pH and log K_{f_1} is the formation constant of 1:1 metal complex. Equation 2 is valid when $T_L \ll T_M$.

Results and Discussion

(*a*) ***Diphenylthiocarbazones and Related Compounds*.** Acid dissociation constants of DPTC, its analogues and formation constants of their 1:1 metal chelates in 50% (v/v) aqueous dioxan are given in Table I. The pK_a data indicate that all the ligands except bis(2,6-dimethylphenyl) and bis(4-methyl-2-nitrophenyl)thiocarbazones are stronger acids than DPTC. This unusual weakly acidic behavior of only the bis(4-methyl-2-nitrophenyl) derivative as compared to other nitro derivatives may be due to the formation of a weak hydrogen bond between the oxygen of nitro group and the proton of NH moiety. On the contrary, bis(2,6-dimethylphenyl)thiocarbazone is found to be

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[†] This paper is dedicated to Professor Henry Freiser, Department of Chemistry, Tuscon, Arizona, on his sixtyfifth birthday.

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Table II. Absorptivity Data for Diphenylthiocarbazone in Chloroform and in 50% (v/v) Aqueous Dioxan at 25 °C

	chloroform			aqueous dioxan			
diarylthiocarbazone	λ_1(max),[a] nm	λ_2(max),[b] nm	ϵ_1/ϵ_2	λ_1(max),[a] nm	λ_2(max),[b] nm	λ_{max},[c] nm	ϵ_1/ϵ_2
diphenyl	605	445	2.3	600	420	500	2.4
bis(2,6-dimethylphenyl)	585	430	2.9	570	415	430	2.1
bis(2-methyl-5-nitrophenyl)	625	440	1.4	605	425	470	0.37
bis(4-methyl-2-nitrophenyl)	690	360	0.20	670	455	540	0.23
bis(2-methyl-4-nitrophenyl)	655	470	1.40	575[d]	450	530	
bis(4-methyl-3-nitrophenyl)	625	440	1.20	610	420	490	0.6

[a] Keto form. [b] Enol form. [c] For anion. [d] Shoulder.

Table III. Absorption Spectra of Metal Complexes in Chloroform at 25 °C

	λ_{max}, nm	
thiocarbazones	Ni(II)	Zn(II)
diphenyl	660, 560, 480, 435 sh	535
bis(2,6-dimethylphenyl)	650, 540, 410	480
bis(2-methyl-5-nitrophenyl)	575, 560, 425	520
bis(4-methyl-2-nitrophenyl)	695, 565, 375	555
bis(2-methyl-4-nitrophenyl)	680, 555, 430	550
bis(4-methyl-3-nitrophenyl)	680, 535, 435	540

a weaker acid than DPTC (as expected) because of the electron-donating effect of methyl groups.

In the case of complexes of nickel(II) and zinc(II) with DPTC and its derivatives, zinc(II) complexes are found to be more susceptible to steric substituents than nickel(II) complexes. This behavior is clearly seen in the case of zinc complexes with bis(*o*-methylphenyl) and bis(2,6-dimethylphenyl)thiocarbazones as compared to DPTC. Complexes of nickel(II) with bis(2-methyl-4-nitrophenyl) and bis(4-methyl-3-nitrophenyl)thiocarbazones show unusually high proton-displacement constants (K_{pd}) but zinc(II) complexes show higher values of K_{pd} only in the case of bis(4-methyl-3-nitrophenyl)thiocarbazones. This indicates that the nitro group does not withdraw electrons from the chelate ring as it can do in the absence of metal ion. This may be attributed to the stereochemical changes around the metal after chelation. Additionally, it can be seen that zinc complexes of bis(2,6-dimethylphenyl)thiocarbazones are found to be more stable than other complexes containing ortho-substituted ligands thus suggesting a tetrahedral geometry for zinc(II) complexes (*2*).

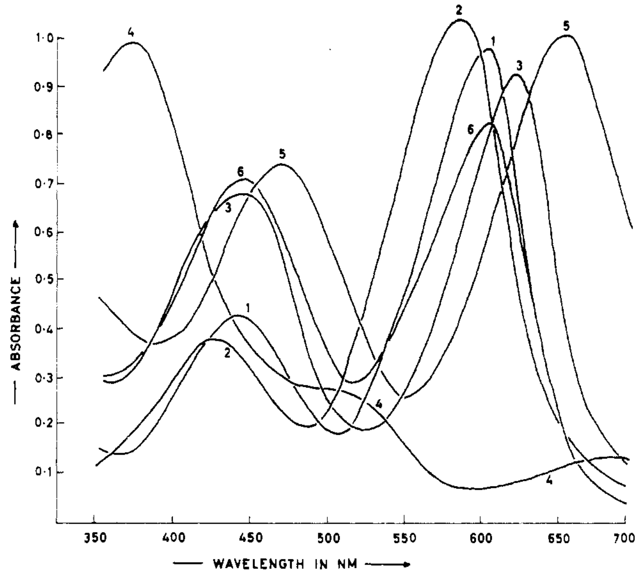

Figure 1. Absorption spectra of diphenylthiocarbazone and substituted diphenylthiocarbazones in chloroform at 25 °C: (1) diphenyl; (2) bis(2,6-dimethylphenyl); (3) bis(2-methyl-5-nitrophenyl); (4) bis(4-methyl-2-nitrophenyl); (5) bis(2-methyl-4-nitrophenyl); (6) bis(4-methyl-3-nitrophenyl).

The absorption spectra of various ligands in chloroform and in 50% (v/v) dioxan-water mixture are respectively shown in Figures 1 and 2 while the absorptivity data are given in Table II. The absorption spectra of ligands in both solvents are found to be very similar. All ligands except bis(4-methyl-2-nitrophenyl)thiocarbazone behave similar to DPTC; the spectra of bis(4-methyl-2-nitrophenyl)thiocarbazones in chloroform exhibit two peaks at 690 and 360 nm with a shoulder band at 520 nm. Of all the ligands only bis(2,6-dimethylphenyl)thiocarbazone peaks are shifted to a lower region while others have a tendency to shift to a higher region. From the absorptivity data given in Table II, it is evident that the ratio ϵ_1/ϵ_2 shows that ligands with nitro substituents favor enolic form. Also, a strong absorption band seen in the lower (enolic form) region of the spectra (see Figure 2) may be due to the greater sensitivity of the nitro group in the high dielectric medium solvent (i.e., aqueous dioxan). Such a behavior was not seen in our earlier studies (*1-4*).

The absorption peaks of nickel(II) and zinc(II) complexes in chloroform are given in Table III. Here again, the spectra of the metal complexes in both chloroform and aqueous dioxan are very similar. In accordance with our earlier observations (*1-4*), nickel(II) complexes exhibit multiple absorption bands characteristic of charge-transfer complexes and zinc(II) complexes show a single intense peak around 500 nm.

(b) Diphenylcarbazones and Related Compounds. The formation constants of DPC and related compounds are given in Table IV. Except bis(2,6-dimethylphenyl)carbazone all the ligands are found to be stronger acids than DPC and this is due to the presence of electron-withdrawing nitro group. It is noticed that the effect of substituents on the pK_a values is additive. Nickel(II) chelates have higher log K_f values than zinc(II) chelates and a small difference exists between log K_{f_1} and log

Table IV. Formation Constants of Metal Diphenyl and Substituted Diphenylcarbazone Complexes at 25 °C and 0.1 Ionic Strength in 50% (v/v) Aqueous Dioxan Medium

		Ni(II)			Zn(II)		K_{pd}	
carbazones	pK_a	log K_{f_1}	log K_{f_2}	log K_{f_3}	log K_{f_1}	log K_{f_2}	Ni(II)	Zn(II)
diphenyl	9.25	6.66	5.98	4.34	6.32	6.12	-2.59	-2.93
bis(2,6-dimethylphenyl)	9.95	5.56	5.00	3.85	5.48	4.75	-4.39	-4.47
bis(2-methyl-5-nitrophenyl)	8.16	5.00			4.70		-3.16	-3.46
bis(4-methyl-2-nitrophenyl)	6.70	5.40	5.25		4.30	3.80	-1.30	-2.40
bis(2-methyl-4-nitrophenyl)	6.80	4.00	3.70		3.50		-2.80	-3.30
bis(*o*-methylphenyl)[a]	9.60	5.67	5.14		5.20	4.78	-3.93	-4.40
bis(*p*-methylphenyl)[a]	9.75	7.55	6.94		7.30	7.13	-2.20	-2.45

[a] Reference *1*.

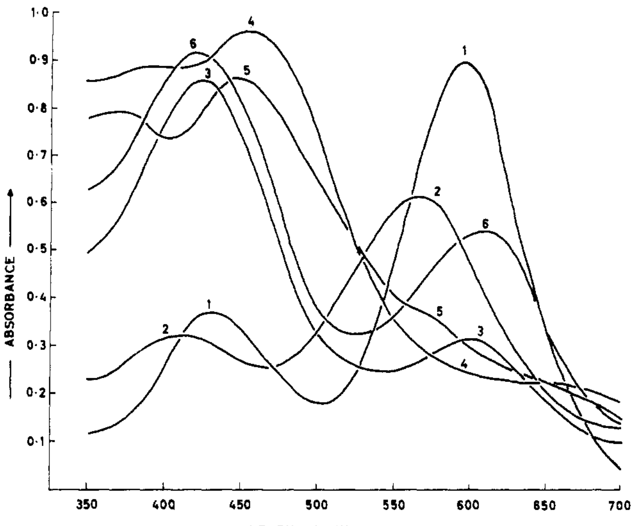

Figure 2. Absorption spectra of diphenylthiocarbazone and substituted diphenylthiocarbazones in 50% (v/v) aqueous dioxan at 25 °C: (1) diphenyl; (2) bis(2,6-dimethylphenyl); (3) bis(2-methyl-5-nitrophenyl); (4) bis(4-methyl-2-nitrophenyl); (5) bis(2-methyl-4-nitrophenyl); (6) bis(4-methyl-3-nitrophenyl).

K_{f_2} values in the case of both the metal chelates. This may be attributed to the fact that the first chelation takes place with partial neutralization of the charge on the central metal ion while the second one completely neutralizes the charge on the central metal ion thereby resulting in the minimum polarity and solvation effect of the metal complex with the medium. Furthermore, due to the octahedral nature of both nickel(II) and zinc(II) complexes, the same steric effect toward ortho substituents is observed. Nickel(II) and zinc(II) complexes of bis(4-methyl-2-nitrophenyl)carbazone possess higher stability in spite of their higher proton displacements constants (K_{pd}). This may be attributed to smaller steric effect of the *o*-nitro group as compared to the *o*-methyl group. One possible explanation would be that the nitro group in the ortho position may orient itself in such a way that it lies out of plane thereby preventing its ability to withdraw electrons by mesomeric effect and thus resulting in increased stability of metal complexes.

Conclusions

In the case of ligands containing sulfur donor atoms (having no steric group), zinc complexes are either almost as stable as or even more stable than the corresponding nickel complexes. However, with ligands containing one oxygen and one nitrogen donor atoms, zinc complexes are either as stable as or even less stable than the corresponding nickel complexes. The ortho-substituted oxygen analogues give significantly weaker complexes with both nickel and zinc, while sulfur-containing ligands give weaker complexes with zinc only. Though the magnitudes of stability orders of zinc and nickel complexes of sulfur and oxygen containing ligands are nearly the same, the proton displacement constants are significantly different. This difference in K_{pd} is due to the higher proton affinity for oxygen than for sulfur in the respective ligands. The higher K_{pd} values make sulfur-donating ligands superior to oxygen analogues because of the formation of complexes at lower pH values.

Registry No. DPTC, 60-10-6; bis(2,6-dimethylphenyl)thiocarbazone, 97234-67-8; bis(2-methyl-5-nitrophenyl)thiocarbazone, 97234-68-9; bis(4-methyl-2-nitrophenyl)thiocarbazone, 97234-69-0; bis(2-methyl-4-nitrophenyl)thiocarbazone, 97234-70-3; bis(4-methyl-3-nitrophenyl)thiocarbazone, 97234-71-4.

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Volumetric Properties of Molten Hydrated Salts. 6. Mixtures of Aluminum Nitrate Decahydrate with Hydrates of Calcium, Cadmium, Zinc, and Magnesium Nitrates

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Densities of the molten binary mixtures of aluminum nitrate decahydrate with hydrates of calcium, cadmium, zinc, and magnesium nitrates were measured at different temperatures and concentrations with a manometric densimeter. Least-squares equations representing densities and molar volumes as a function of temperature are given. The molar volumes of mixtures were additive. Composition variations of α and V_E are explained by considering the complexing nature of the ions.

Introduction

Volumetric behavior of molten hydrated salts has been studied (*1*–*10*) to understand ion–water interactions over the concentration region where solution studies were uncommon. Additivity of volumes is a good approximation to understand the different types of volumetric behavior. The amount of water present in the hydrated salts remains in the form of coordinated and lattice water, perturbed by ionic distribution (*11*, *12*). In continuation of our studies of molten hydrated salts (*3*, *7*–*10*), the results of density measurements of binary molten hydrates of aluminum nitrate with calcium, cadmium, zinc, and magnesium nitrates are reported in this paper.

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