

Formation Constants of Adducts of Some Zinc Oxinate Chelates with Nitrogen Bases

VIJAYA M SHIRSAT & KASHINATH S BHATKI*

Chemistry Division, Bhabha Atomic Research Centre,
Trombay, Bombay 400 085

Received 10 June 1985; revised and accepted 12 August 1985

It is shown that in a monophasic devoid of water the adducts formed by pyridine type bases with zinc oxinate are actually hexacoordinated and contain two molecules of adduct-forming ligand. A modified formula has been employed to confirm this finding. This is in contrast to a penta-coordinate adduct reported by Chou and Freiser [*Anal Chem*, **40** (1968) 34] and recently supported by Rane and Nepali [*Indian J Chem*, **24A** (1985) 158].

Chou and Freiser¹, employing solvent extraction technique, studied adduct formation of zinc chelates of oxine (8-quinolinol) and its analogues such as 2- and 4-methyl derivatives with nitrogen bases. They used organic bases like pyridine and its methyl analogues such as picolines, lutidines and collidines to study the steric hindrance caused by the methyl group(s) in various positions in the pyridine ring. Because of the steric hindrance of the methyl groups in 2- and 6-positions, e.g. in the case of 2, 6-lutidine or 2, 4, 6-collidine, the adducts formed were very weak as revealed by their low adduct formation constants. In most of these adducts Chou and Freiser¹ observed 1:1 stoichiometry (zinc oxinate-base), instead of 1:2 normally expected and suggested a pentacoordinate structure for these adducts—a square base pyramidal geometry, in which the zinc oxinate occupied the base of the pyramid with one molecule of the nitrogen base occupying the position at the apex of the pyramid.

Later Rane and Nepali² repeated the work of Chou and Freiser using spectrophotometry and arrived at the same conclusion as that postulated by Chou and Freiser¹. Rane and Nepali² determined the stoichiometry of the adducts from the slopes of the linear plots of $\log(A_0 - A/A)$ versus the log concentration of the base, and the adduct formation constants from the intercepts of such plots.

We believe that in the systems studied by Chou and Freiser¹, employing solvent extraction technique, because of the large amount of the aqueous phase the sixth coordination site in the extracted adduct is occupied by a water molecule giving the adduct complex a hexacoordinated octahedral structure. There is no way, however, to ascertain the presence of water molecule. As Rane and Nepali² carried out the

entire spectrophotometric work in a monophasic it was easy for them to show whether the adduct was really pentacoordinated one or the sixth site was occupied by a molecule of water.

We undertook the work³ even before Rane and Nepali published their results but we followed the method described by Vogel⁴ meticulously to remove water completely from chloroform which was employed as the monophasic in our spectrophotometric work, which was carried out employing HITACHI-330 spectrophotometer. This instrument was calibrated before use with solutions of potassium chromate and copper sulphate.

The formula employed by Rane and Nepali to find out the stoichiometry of the adduct and the adduct formation constant was found to be unsuitable for the zinc system under study, since at the wavelength (368 nm) at which the adduct formation reduced the absorbance due to the simple chelate alone did not show either a negligible or zero value on complete formation of the zinc adduct. This difficulty did not arise in the case of nickel oxinate chelate and hence was successfully applied⁵ to that system. Under the circumstance a modified version³ of the same (see Eq. 1) was used to calculate the results where the descending portion of the absorption curve was not used for calculation, instead we used that part of the spectrum where the absorbance went on increasing due to adduct formation on addition of the base ($\lambda_{\max} = 382 \text{ nm}$).

$$\log \frac{A_i - A_0}{A_n - A_i} = -n \log B + \log K_{AD} \quad \dots (1)$$

where A_i stands for the absorbance of the solution containing both the chelate and the adduct as the absorbing species, A_0 represents the absorbance of the chelate solution alone in the absence of any base, and A_n , the absorbance of the solution in which the adduct formation is complete with no contribution from any simple chelate.

The results calculated from the modified Eq. (1) are presented in Table 1. It is significant to note that in the case of the zinc quinaldinate system where 1:1 adducts were formed the results agreed quite well with those of Chou and Freiser in spite of the fact that the methods were different—two-phase solvent extraction and the monophasic spectrophotometry. In the case of zinc oxinate adducts, however, our results are very close to those of Chou and Freiser. It is interesting to note that our data indicated 1:2 stoichiometry suggesting a

Table 1—Comparison of Adduct Formation Constants for Zinc Chelate System

Base	log K_{AD}^*			log $K_{AD}^\dagger$		
	Rane <i>et al</i>	Chou <i>et al</i>	Shirsat & others	Rane <i>et al</i>	Chou <i>et al</i>	Shirsat & others
Pyridine	1.07	3.05	3.90	0.22	1.60	1.30
2-Picoline	0.66	2.10	2.95	-0.24	1.00	1.08
4-Picoline	1.50	3.40	4.90	0.60	1.75	1.66
2,4-Lutidine	0.75	—	2.80	-0.33	—	—
2,6-Lutidine	No adduct	—	0.60	No adduct	—	—
2,4,6-Collidine	0.92	1.50	3.20	-0.15	0.20	—
1,10-Phenanthroline	3.75	—	7.80	2.52	—	3.35
2,9-Neocupr	2.30	—	3.10	1.58	—	2.70
2,2'-Bipyridyl	2.14	—	5.7	2.44	—	3.25
Ethylenediamine	—	—	7.6	—	—	—

*8-Quinolinel chelate.

†8-Quinaldine chelate.

hexacoordinated octahedral configuration as expected by theory against the observations of Rane and Nepali², who, using a similar technique concluded that in a monophasic system most of the adducts were penta-coordinated. This decisively proves that the formula employed here is more appropriate to the zinc oxinate system and that the complexes formed by pyridine-type nitrogen bases with zinc oxinate are hexacoordinated having an octahedral structure.

References

- 1 Chou F C & Freiser H, *Anal Chem*, **40** (1968) 34.
- 2 Rane A T & Nepali D R, *Indian J Chem*, **24A** (1985) 158.
- 3 Shirsat V M & Bhatki K S, *Inorg Chem*, (Communicated).
- 4 Vogel A I, *Text Book of practical organic chemistry 4th ed.* (Longman, England), 1978, p. 268.
- 5 Bhatki K S, Rane A T & Freiser H, *Inorg Chim Acta*, **26**(1978) 183.