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An Evaluation of the Donor Properties of s-Triazine

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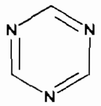
The high sensitivity of the aromatic N-heterocycle s-triazine (trz) towards hydrolytic attack [1] has prevented a quantitative estimation of its basic properties from being achieved, at least as reflected by an acid dissociation constant The pK_a of its conjugate acid calculates as –3 1 using the method of Clark and Perrin [2], suggesting that its electron donor properties may be quite low We have prepared a series of complexes of s-triazine with bivalent cobalt salts whose properties are somewhat analogous to the corresponding complexes of pyridine and like bases, although often the s-triazine products are stable only at low temperature and in the absence of moisture [3]

In a further attempt to estimate the donor power of the substance the 1 1 formation constant for the addition of s-triazine to bis(ethylacetoacetato)copper (II) in benzene was determined, since similar data for a number of N-heterocyclic monodentate bases is available for comparison [4] Details of that estimation are outlined below



(trz)

Experimental

Spectrophotometric determination of the equilibrium constant for the formation of the 1 1 adduct was carried out using the method of Graddon and Watton [4] The combination of reference Lewis acid (β-diketonate) and solvent adopted was influenced by earlier experience [4] that such a system would provide larger formation constants than other possible combinations Solutions which were 2 5 X 10^{-3} *M* with respect to the copper chelate and which varied from 1 25 X 10^{-2} to 4 0 X 10^{-1} *M* with respect to s-triazine were used

The extinctions of the solutions were determined at 680 nm Equilibrium concentrations of the various species were calculated assuming a linear relationship between the observed extinction and the mol fraction of the copper present as adduct according to the relationship

$$[\text{adduct}] = [\text{total copper}]\,\frac{\epsilon - \epsilon_0}{\epsilon_\infty - \epsilon_0}$$

where values of ϵ_0 and ϵ were experimental and the value of ϵ_∞ was that found, by trial and error, to give the most reproducible values of the equilibrium constant K

The experimental data for the equilibrium studies are given in Table I Absorption spectra and equilibrium constants were determined using a Unicam SP500 spectrophotometer at 20 °C Analytical reagent grade benzene solvent was dried over anhydrous potassium carbonate before use

TABLE I Equilibrium Constant Data for Formation of Bis-(ethylacetoacetato)copper(II)/s-Triazine Adduct in Benzene

ϵ	Equilibrium Concentrations (mmol cm^{-3})			K^c (mol^{-1})
	s-Triazine	Adduct	$Cu(acest)_2$	
35 2^a	0 00	0 00	2 50	–
37 2	12 12	0 38	2 12	14 8
38 6	24 36	0 64	1 86	14 1
39 8	36 63	0 87	1 63	14 6
40 4	49 02	0 98	1 52	13 2
42 6	98 55	1 45	1 05	14 0
44 2	148 30	1 70	0 80	14 3
45 0	198 15	1 85	0 65	14 4
46 0	297 95	2 05	0 45	15 3
46 4	397 88	2 12	0 38	14 0
48 4^b	∞	2 50	0 00	–

$^a\epsilon_0$ $^b\epsilon_\infty$ $^c\bar{K}$ = 14 3 ± 0 3 mol^{-1} (90% confidence limits)

Results and Discussion

The 1 1 stoichiometry of the formation reaction was shown clearly by a well defined isosbestic point (Figure 1) and an equilibrium constant which is highly consistent over a wide range of base concentration The formation constant was determined as 14 3 ± 0 3 mol^{-1} (to 90% confidence limits) This compares with the values obtained for the pyridine (K = 29 0 ± 1 0) and 4-methylpyridine (K = 58 7 ± 3 8) adducts by the same method [4] The ionization constants of these two bases are $pK_{a(py)}$ = 5 25 and $pK_{a(4\text{-mepy})}$ = 6 03 respectively [5]

The results indicate that the triazine molecule is intrinsically a weaker Lewis base than either of the other two, and if the entropy of adduct formation may be assumed to be independent of the base involved then it is also the weakest donor of the

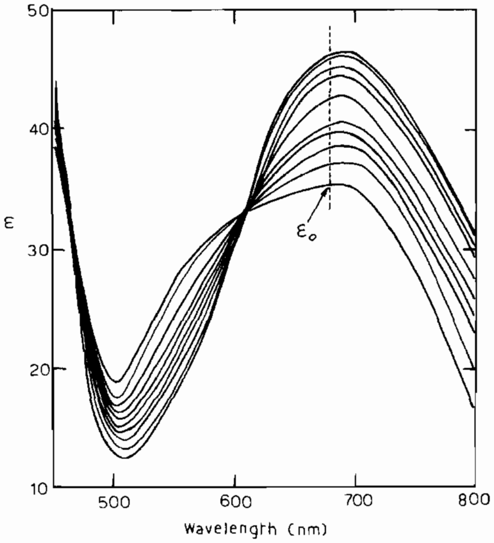


Fig. 1. Visible absorption spectra of bis(ethylacetoacetato)-copper(II)/s-triazine solutions in benzene.

three. The value obtained for the formation constant, however, does suggest that s-triazine has a significant degree of basic character, and would be expected to form 1:1 adducts more thermodynamically stable than the sterically hindered base 2-methylpyridine whose adduct formation constant was determined as 9.6 ± 0.3 mol^{-1} in this Cu–β-diketonate system [4].

A green solid product was isolated from the s-triazine adduct formation reaction. However this proved to be extremely unstable in air and was not characterized. Such behaviour is typical of the metal complexes that form with s-triazine [3] and it is thought that this instability is due to the reaction of the coordinated base molecule with atmospheric moisture to form a "covalent hydrate" species [1, 3, 6, 7].

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