

***N*-BASES AS SYNERGIZING AGENTS IN THE SOLVENT EXTRACTION OF
⁶⁴Cu AND ⁶⁵Zn BY THENOYLTRIFLUOROACETONE***

By R. DRIVER† and W. R. WALKER†

Synergistic extraction in systems such as M/HTTA/Sy [M = Cu²⁺ or Zn²⁺; HTTA = thenoyltrifluoroacetone; Sy = an organophosphorus compound (e.g. tri-*n*-octylphosphine oxide), quinoline, isoquinoline, pyridine, etc.] has been investigated in recent years. Ternary complexes of the type M(TTA)₂Sy_x (*x* = 1 or 2) have been studied in solution and some have been isolated.¹⁻⁴ Casey and Walker⁵ have noted the order of synergistic extraction of ⁶⁴Cu by acetylacetone and certain *N*-bases. The present study is relevant to the above and concerns the extraction of ⁶⁴Cu and ⁶⁵Zn by HTTA and a series of *N*-bases.

TABLE 1
EXTRACTION OF M²⁺/HTTA/*N*-BASE

Base	M = ⁶⁴ Cu		M = ⁶⁵ Zn	
	10 ² <i>C</i> (M)	<i>K</i> _d	10 ² <i>C</i> (M)	<i>K</i> _d
Pyridine	2.53	135	2.43	5.9
2-Methylpyridine	2.57	400	1.70	1.9
3-Methylpyridine	2.27	459	2.04	31.0
4-Methylpyridine	2.49	581	1.83	49.8
Quinoline	1.81	261	2.40	2.1
Isoquinoline	2.09	505	2.08	88.0
4-Ethylpyridine	2.00	392	1.75	163.0
4-Cyanopyridine	2.03	109	2.01	0.04
2-Benzoylpyridine	1.89	45	2.30	0.1
4-Hydroxypyridine	2.03	12	2.30	0
2-Aminopyridine	—	—	2.00	4.7

Experimental

The extraction technique has been described previously.^{1,2} The liquid *N*-bases were redistilled where necessary and the solids (4-cyano-, 4-hydroxy-, and 2-amino-pyridine) were used as supplied. The ⁶⁴Cu and ⁶⁵Zn were prepared by the Isotopes Division, A.A.E.C., Lucas Heights,

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† Department of Chemistry, University of Newcastle, N.S.W. 2308.

¹ Curthoys, G. C., and Walker, W. R., *Aust. J. Chem.*, 1967, **20**, 2541 and references therein.

² Casey, R. J., Fardy, J. J. M., and Walker, W. R., *J. inorg. nucl. Chem.*, 1967, **29**, 1139.

³ Graddon, D. P., and Weeden, D. G., *Aust. J. Chem.*, 1963, **16**, 980.

⁴ Graddon, D. P., and Weeden, D. G., *Aust. J. Chem.*, 1964, **17**, 607.

⁵ Casey, R. J., and Walker, W. R., *J. inorg. nucl. Chem.*, 1967, **29**, 1301.

N.S.W. Due to the short half-life of ^{64}Cu , work with this tracer was carried out at Lucas Heights, counting being done with an Ekco Electronics N550A γ -ray scintillation counter. The samples were shaken for 2 hr. For ^{65}Zn extractions, the samples were shaken for 24 hr and counted as described earlier.¹ The hexane phase contained $2 \times 10^{-3}\text{M}$ HTTA and c. $2 \times 10^{-2}\text{M}$ *N*-base. The aqueous phase containing the tracer was a sodium acetate-acetic acid buffer, pH 5.70. The results are shown in Table 1.

Discussion

The extractions with both ^{64}Cu and ^{65}Zn were carried out under similar conditions so that their extractabilities, as well as the order of synergistic extraction of the *N*-bases, could be compared. In the case of ^{64}Cu , the extractions were so high that the statistics of counting were not good. The results for ^{65}Zn , however, are sufficiently accurate to be critically discussed.

The greater extraction in the copper system compared to that of zinc is probably due to the stability of ternary complexes. As shown by Ke and Li,⁶ the stabilities of ternary copper(II) complexes such as $\text{Cu}(\text{TTA})_2\text{Sy}$ (Sy = organophosphorus compound) are much greater than for the corresponding zinc complexes.

The order 4-methylpyridine > 3-methylpyridine > pyridine is as expected from the basic strength of the bases.⁷ For the same reason, 2-methylpyridine should also extract better than pyridine. However, steric hindrance by the methyl group explains its poor coordinating ability and hence the anomalously low extraction. Isoquinoline extracts better than quinoline, probably because of its greater basicity and less steric hindrance. Irving and Al-Niaimi⁸ have confirmed that isoquinoline forms stronger adducts with copper(II) β -diketonates than does quinoline. The superior extraction of isoquinoline to that of the picolines is not to be expected from their relative basic strengths, but can be explained in terms of water solubilities. The picolines are much more soluble and the proportion of $\text{Zn}(\text{TTA})_2\text{B}_x$ (B = *N*-base) in the hexane phase will be greater, if B is largely partitioned in this phase.

The lack of extraction by 4-hydroxypyridine is not surprising. Casey and Walker⁵ reported that in the system Cu/Hacac/4-hydroxypyridine, $K_d = 6.5$ and $K_d^0 = 8.0$. This could be called "anti-synergism". Apparently hydrogen bonding of 4-hydroxypyridine with water does not favour the formation of a ternary complex in the organic phase. Although 2-aminopyridine is insoluble in hexane, it shows a similar extraction to pyridine. The steric hindrance caused by the amino group in the 2-position must be counteracted by its greater basic strength.

The most surprising result of this work is the high extraction shown by 4-ethylpyridine which is even greater than for isoquinoline. The former, although water-soluble, apparently forms an adduct that is soluble in hexane. Casey and Walker⁵ observed a similar result when acetylacetone was the extracting chelate. The same authors further showed that in the system Cu/Hacac/B, the order of synergistic extractions was pyridine > 4-cyanopyridine > pyridine > 2-benzoylpyridine > 4-hydroxypyridine. This has been indicated in the present study which

⁶ Ke, C. H., and Li, N. C., *J. inorg. nucl. Chem.*, 1966, **28**, 2255.

⁷ Sacconi, L., Lombardo, G., and Pacletti, P., *J. inorg. nucl. Chem.*, 1958, **8**, 217.

⁸ Irving, H. M. N. H., and Al-Niaimi, *J. inorg. nucl. Chem.*, 1965, **27**, 1671.

also confirmed the importance of the role of the stability and the solubility of ternary complexes in solvent extraction.

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