

able hydrogen and the co-ordination of the negative O⁻ with metals.

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1. Shukla, P., Khare, M. P. and Srivastava, L. N., *Z. Anorg. Allg. Chem.*, 1964, **333**, 165.
2. Nyholm, R. S., *J. Chem. Soc.*, 1957, p. 1714.

COMPOSITION AND STABILITY OF METAL-4-(2-PYRIDYLAZO) RESORCINOL CHELATES OF VANADIUM, NIOBIUM AND TANTALUM

IN continuation of the previous work^{1,2} reported from these laboratories on the chelates of 4-(2-pyridylazo) resorcinol (PAR), the chelates of vanadium, niobium and tantalum have been described. The compositions were found to be as 1:1 by employing the method of continuous variations and the mole ratio method, the V-PAR being studied at 550 m μ (pH 5.0), Nb-PAR at 540 m μ (pH 6.0) and Ta-PAR at 500 m μ (pH 6.0). The absorption spectra of the complexes were studied by Vosburgh and Cooper's method³ which indicated the λ_{\max} at 550 m μ for the vanadium, 540 m μ for niobium and 500 m μ for tantalum chelates. The λ_{\max} of PAR was found to be 400 m μ at pH 5.0 and 410 m μ at pH 6.0.

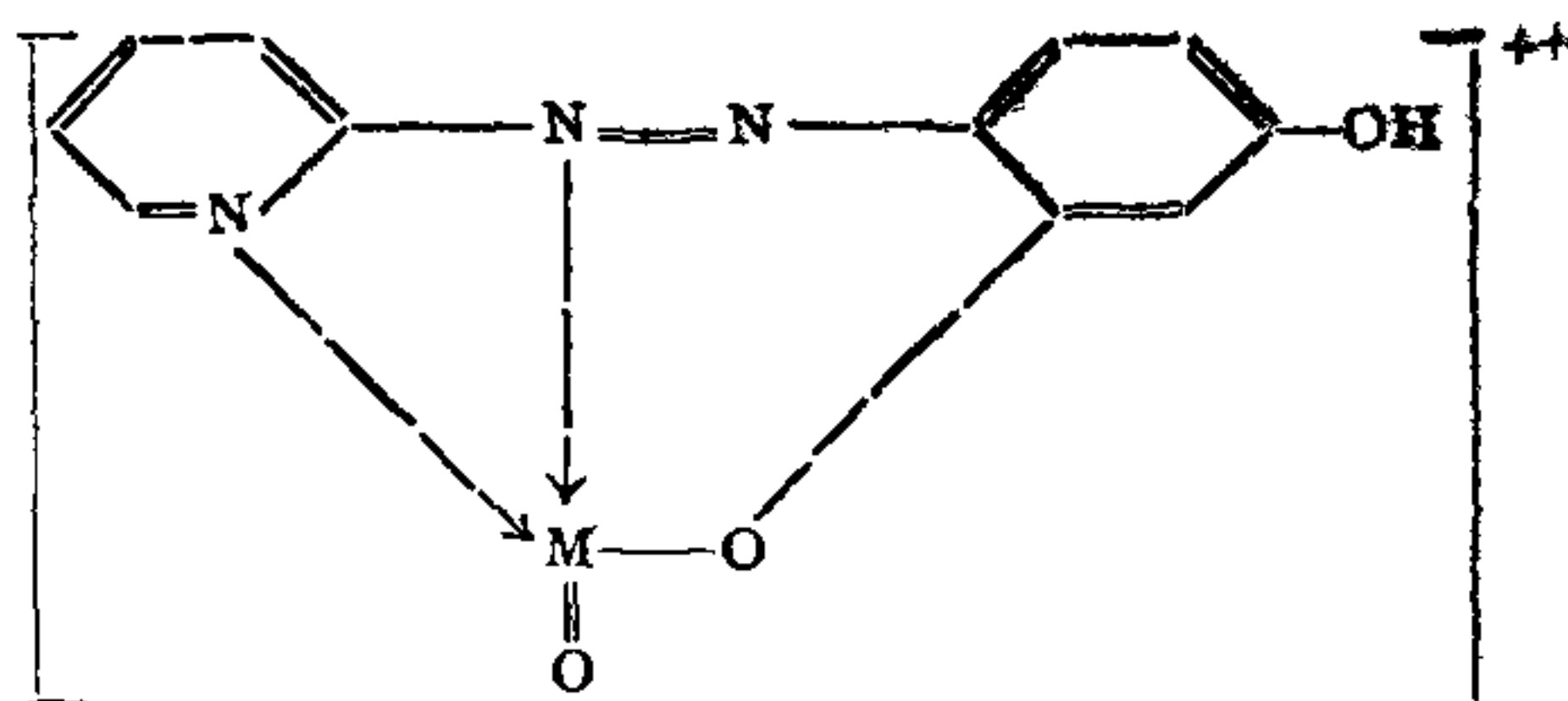
The values of stability constants have been determined by different methods and are given in Table I.

TABLE I
Stability constants of chelates at 25° C.

Chelate	pH	log K	Method
V - PAR	5.0	4.2 ± 0.1	(i)
		5.2 ± 0.1	(ii)
		4.6 ± 0.1	(iii)
Nb - PAR	6.0	4.3 ± 0.1	(i)
		4.5 ± 0.2	(ii)
		4.7 ± 0.0	(iii)
Ta - PAR	6.0	4.5 ± 0.1	(i)
		4.7 ± 0.1	(ii)
		4.8 ± 0.1	(iii)

Methods (i), (ii) and (iii) correspond to the method of Dey and associates, Job's method of continuous variations and Mole ratio respectively.

A tentative suggestion for the structure of 1:1 chelates of vanadium, niobium and tantalum with PAR has been given on the evidence that the chelates are cationic as found by electrophoresis experiments. The structure proposed is



M stands for V, Nb and Ta

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Allahabad, June 20, 1967.

1. Dwivedi, C. D., Munshi, K. N. and Dey, A. K., *J. Inorg. Nucl. Chem.*, 1966, **28**, 245.
2. Munshi, K. N. and Dey, A. K., *Analyt. Chem.*, 1964, **36**, 2003.
3. Vosburgh, W. C. and Cooper, G. R., *J. Am. Chem. Soc.*, 1941, **63**, 437.

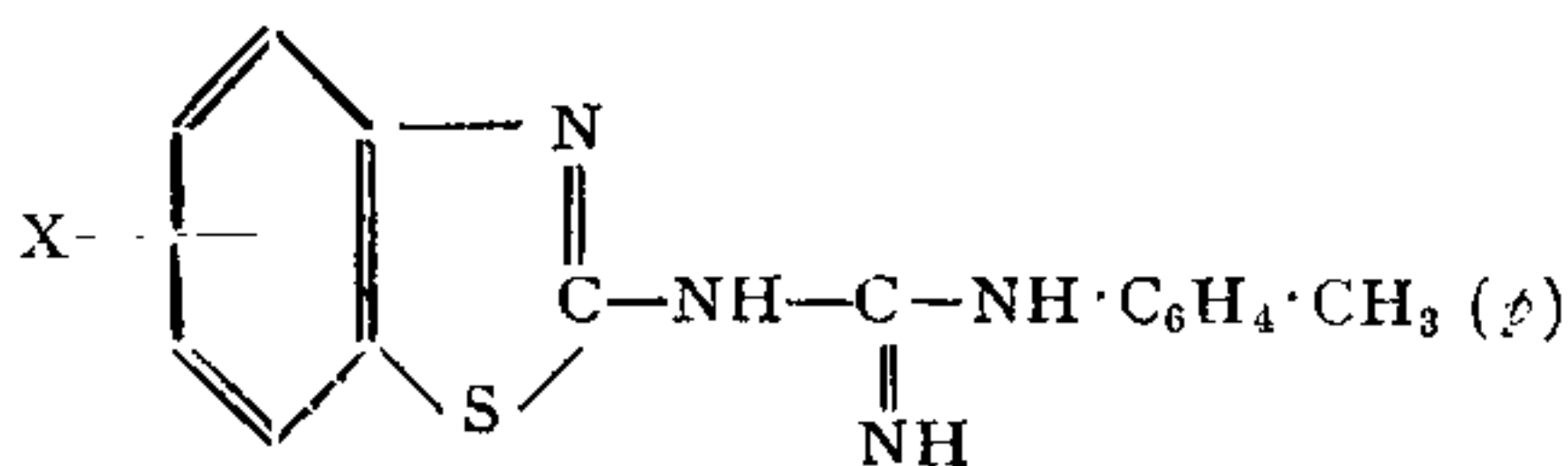
SOME NEW N-p-TOLYL-N'-2- (SUBSTITUTED) BENZOTHAZOLYL GUANIDINES

CERTAIN substituted diguanides have shown antimalarial¹ activity which created interest in searching for other therapeutically useful members of this series and in due course led to the discovery of high antibacterial activity,² more commonly among a series of biguanides. Recently, Bhargava *et al.*³⁻⁴ have synthesized several N-aryl-N'-2-benzothiazolyl guanidines and have shown that the hydrochlorides of these bases are more active against gram-positive bacteria as compared to gram-negative ones. This led the authors to synthesize some new diaryl guanidines in which one aryl group is p-tolyl and another a substituted benzothiazolyl group.

In this communication 2-amino-(substituted) benzothiazoles⁵⁻⁷ were condensed with p-tolyl-isothiocyanate.⁸ The resulting benzothiazolyl thiocarbamides⁹ were desulphurized using lead oxide in ethanolic ammonia. The general method followed for preparing the guanidines is illustrated by the following example.

N-p-tolyl-N'-2-(4-chloro)-benzothiazolyl thiocarbamide (3 g.), yellow lead oxide (5 g.) and strong ethanolic ammonia (25 ml.) were heated in a sealed glass tube in a water-bath for 3-4 hours. Lead sulphide was filtered while hot and the N-p-tolyl-N'-2-(4-chloro)-benzothia-

TABLE I
N-p-Tolyl-N'-2-(substituted) benzothiazolyl guanidines



Sl. No.	Nature of substituent X	Yield %	M.P. °C.	Mol. Formula	Nitrogen %		Sulphur %	
					Found	Reqd.	Found	Reqd.
1	4-Chloro-	65	204	C ₁₅ H ₁₃ N ₄ SCl	17.54	17.69	10.15	10.11
2	5-Chloro-	70	196	C ₁₅ H ₁₃ N ₄ SCl	17.78	17.69	10.20	10.11
3	6-Chloro-	90	171	C ₁₅ H ₁₃ N ₄ SCl	17.65	17.69	10.04	10.11
4	6-Bromo-	60	159	C ₁₅ H ₁₃ N ₄ SBr	15.59	15.52	8.80	8.86
5	6-Methoxy-	35	162	C ₁₆ H ₁₆ N ₄ SO	17.93	17.95	10.19	10.25
6	4-Ethoxy-	45	188	C ₁₇ H ₁₈ N ₄ SO	17.30	17.18	9.76	9.81
7	6-Ethoxy-	40	160	C ₁₇ H ₁₈ N ₄ SO	17.25	17.18	9.93	9.81

zoyl guanidine obtained from the filtrate was crystallised from ethanol. The yields, melting points and analytical results, etc., of the various guanidines are given in Table I.

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1. Curd, F. H. S. and Rose, F. L., *J. Chem. Soc.*, 1946, p. 729.
2. Rose, F. L. and Swain, O., *Ibid.*, 1956, p. 4422.
3. Bhargava, P. N. and Devi, K. S., *J. Ind. Chem. Soc.*, 1963, **40**, 868.
4. — and Ram, P., *Indian J. Chem.*, 1966, **4**, 95.
5. Hegerschoff, *Ber. Dtsch. Chem. Ges.*, 1903, **36**, 3221.
6. De Clermont, *J. Chem. Soc.*, 1877, p. 70.
7. Bhargava, P. N. and Baliga, B. T., *J. Ind. Chem. Soc.*, 1958, **35**, 807.
8. Vogel, A. I., *A Text-Book of Practical Organic Chemistry*, Longmans, Green & Co., London, 1954, p. 615.
9. Bhargava, P. N. and Ram, P., *Indian J. Appl. Chem.*, 1961, **24**, 181.

DISTRIBUTION OF TITANIUM IN COEXISTING PYROXENES FROM THE KONDAPALLI CHARNOCKITES

THE purpose of this note is to observe the nature of distribution of titanium in the coexisting (ortho- and clino-) pyroxenes from the charnockitic rocks of Kondapalli and Madras, and to understand the causes for the observed distribution.

Eight Kondapalli pyroxene pairs were separated from their host rocks by following the usual techniques¹ and these purified mineral

concentrates were chemically analyzed and their titanium content was determined colorimetrically. The data thus obtained, together with that available for ten Madras pyroxene pairs,²⁻⁴ are presented in Table I. The weight

TABLE I

Sample No.	Wt. % TiO ₂	
	Orthopyroxene	Clinopyroxene
Kondapalli		
323	0.27	0.69
D14	0.43	0.43
28	0.38	0.41
61	0.26	0.48
G17	0.24	0.35
474	0.28	0.43
62	0.38	0.40
A18	0.30	0.43
Madras*		
3709	0.10	0.68
4645	0.15	0.72
Ch. 114	0.19	0.38
2270	0.15	0.24
2941	0.30	0.70
Ch. 132	0.20	0.32
Ch. 199	0.17	0.44
4642 A	0.11	0.30
Ch. 207	0.14	0.25
115	1.02	0.85

* Data from Howie,² Howie and Subramaniam,³ and Subramaniam.⁴

per cent TiO₂ in orthopyroxene, chosen as a measure of concentration of the element, is plotted against the weight per cent TiO₂ in clinopyroxene on a graphical log-log plot (Fig. 1) for all these eighteen pyroxene pairs. Lines of equal distribution coefficient (K_D) have a 45° slope on such a plot and the line drawn represents K_D = 1. TiO₂ is more in clinopyroxene than in the coexisting orthopyroxene in seventeen pairs, while the reverse is observed in only one Madras pair; the distribution point