

and coordination numbers of atoms in the surface layer are claimed to play a major role (5).

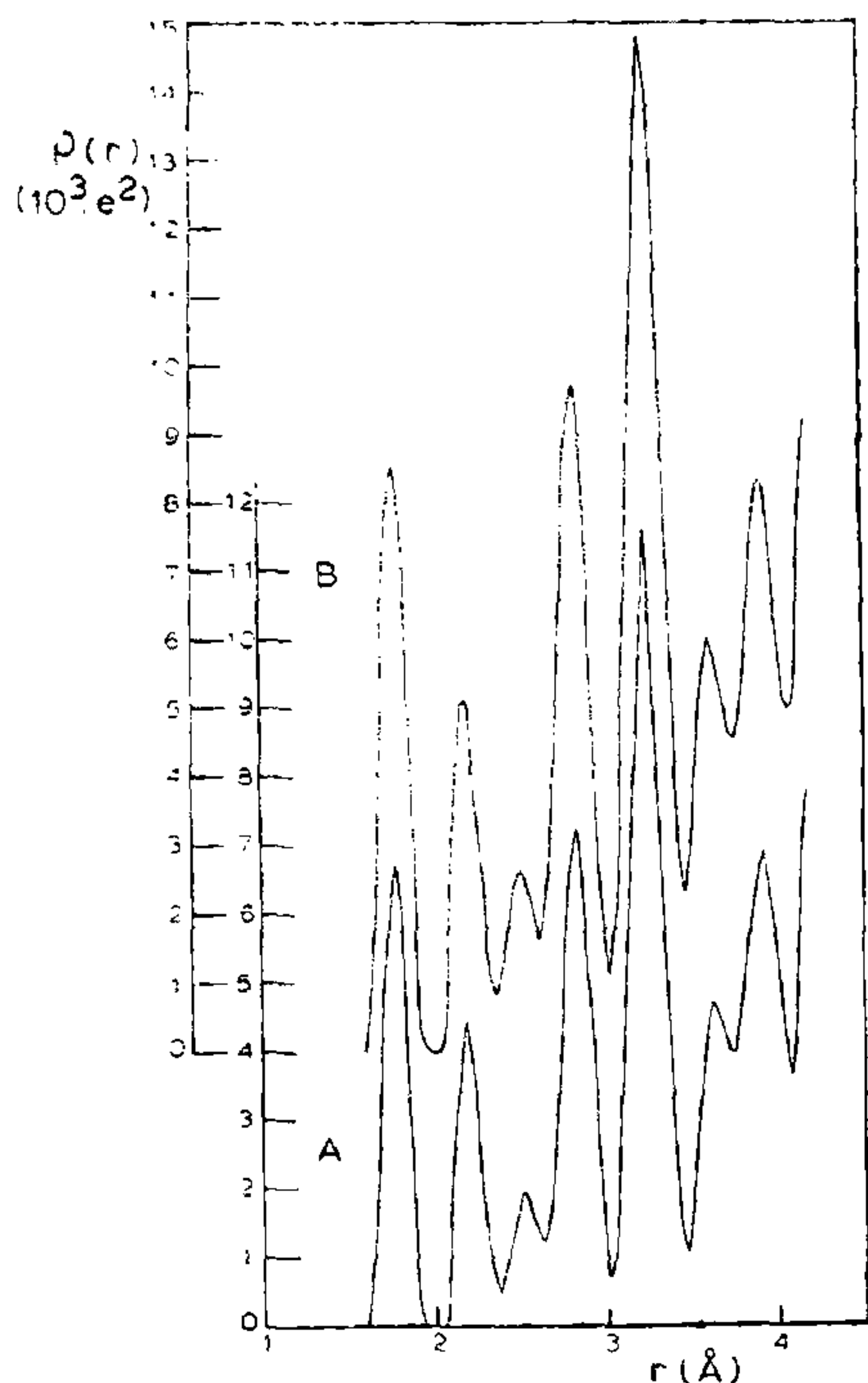


FIG. 2. Radial electron distribution of catalysts A and B.

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Belgium, September 30, 1971.

1 a. Mann, R. S., *Indian J. Technol.*, 1965, 3, 53.

b. Rav, N., Murad, K. M., Anand, K. S. and Nyogi, R. K., *Petroleum and Hydrocarbons (India)*, 1971, 5, 148.

2 a. Leonard, A. J., Van Cauwelaert, F. and Fripiat, J. J., *J. Phys. Chem.*, 1967, 71, 695.

b. Ratnasamy, P. and Leonard, A. J., *Catalysis Reviews* (In press).

3. Vogel, A. I., *A Text-book of Quantitative Inorganic Analysis*, Longmans, 1961.

4. Cahen, R. M., Marechal, J. E. M., della Faille, M. P. and Fripiat, J. J., *Anal. Chem.*, 1965, 37, 133.

5. Balandin, A. A., *Adv. Catalysis*, 1958, 10, 96.

ESTIMATION OF METAL COMPLEXES OF THIOSEMICARBAZIDE WITH CHLORAMINE-T

THIOSEMICARBAZIDE (TSC) has been known as a useful complexing agent for metallic ions. This compound can be conveniently estimated by its reaction with chloramine-T (CAT) under specified conditions¹ and the method was found to be useful in estimating two metal complexes $\text{Zn}(\text{TSC})_2\text{SO}_4$ and $\text{Ni}(\text{TSC})_2(\text{NO}_3)_2$. It was thought to be of interest to extend the method to other metal complexes of TSC. The present communication reports the preparation and oxidation of some TSC complexes of zinc group of metals and a transition metal complex $\text{Ni}(\text{TSC})_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ with CAT.

Materials and method.—E Merck TSC was purified by recrystallization. Triple distilled water was used for preparing the solutions. Approximately decinormal CAT solution (E Merck sample) was standardized by the iodometric method. All other reagents were of accepted grades of purity. Zinc perchlorate solution was prepared by slowly dissolving A.R. zinc in 9 N HClO_4 until the reaction stopped. The excess zinc was then filtered off. Standard buffer systems² were employed for preparing solutions of complexes.

I.R. spectra of the complexes were recorded on a Carl Zeiss UR-10 spectrophotometer. KBr disc technique was employed.

Complexes $\text{Zn}(\text{TSC})_2(\text{NO}_3)_2$, $\text{Zn}(\text{TSC})_2(\text{ClO}_4)_2$, $\text{Cd}(\text{TSC})_2\text{Cl}_2$ and $\text{Hg}(\text{TSC})_2\text{Cl}_2$ were obtained by mixing aqueous solutions of TSC and the corresponding salt in the molar ratio 2:1. The resulting solution was slowly evaporated at 60° on a water-bath and then cooled in ice, when crystals of the complex appeared. Crystals of $\text{Cd}(\text{TSC})_2\text{SO}_4$ were obtained by simply scratching the sides of the beaker containing the mixture, while $\text{Ni}(\text{TSC})_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ crystallized as pinkish violet needles when the mixture was kept in a desiccator for 2-3 hours. In all cases, the complexes were purified by recrystallization from warm water.

The elemental composition of the complexes was determined by microanalyses.

The nature of metal-ligand bonding in the complexes was established by comparing their I.R. spectra with the spectrum of TSC^{3-5} . This compound has N-H stretching frequencies at 3389, 3285 and 3194 cm^{-1} . On complexation, the bands at 3389 and 3194 cm^{-1} slightly shift to lower frequencies, while a small upper shift is noticed with the 3285 cm^{-1} band. The strong band at 800 cm^{-1} in TSC is attributed

TABLE I
Oxidation of metal complexes of thiosemicarbazide with chloramine-T

Zn (TSC) ₂ (NO ₃) ₂		Zn (TSC) ₂ (ClO ₄) ₂		Cd (TSC) ₂ Cl ₂		Cd (TSC) ₂ SO ₄		Hg (TSC) ₂ Cl ₂		Ni (TSC) ₂ SO ₄ ·3H ₂ O	
Amount taken mg	Amount found mg	Amount taken mg	Amount found mg	Amount taken mg	Amount found mg	Amount taken mg	Amount found mg	Amount taken mg	Amount found mg	Amount taken mg	Amount found mg
1.9	2.0	3.1	3.0	1.2	1.2	2.2	2.3	0.8	0.8	1.6	1.7
4.9	4.8	6.1	6.1	3.1	3.0	5.4	5.3	2.1	2.0	4.1	4.1
6.8	6.8	9.2	9.1	6.1	6.1	7.6	7.5	2.9	2.8	7.6	7.6
9.7	9.8	12.2	12.1	9.2	9.2	10.8	10.9	4.1	4.3	8.1	8.3
14.6	14.8	15.3	15.1	12.2	12.1	16.2	16.0	6.2	6.2	12.1	12.1
19.5	19.8	18.3	18.2	18.3	18.1	21.6	21.7	10.2	10.0	16.3	16.3
24.3	24.6	24.4	24.2	24.4	24.2	27.0	27.1	30.6	30.4

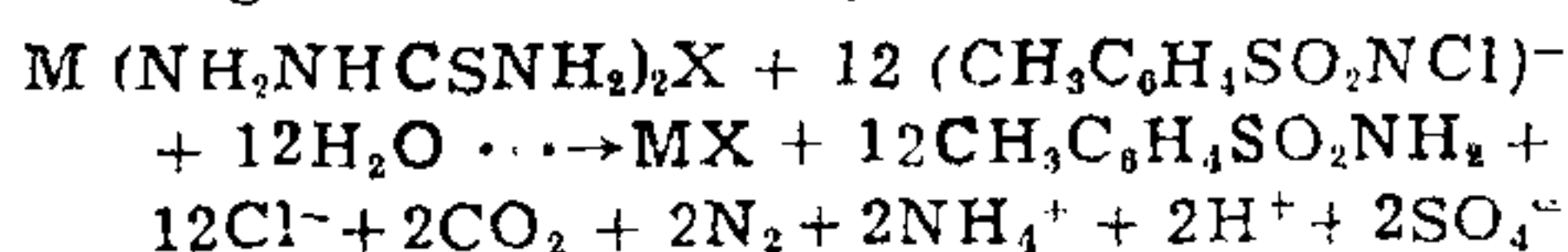
to pure $\nu_{\text{C-S}}$ (stretch)³, but it could be a combination band of $(\nu_{\text{C-S}} + \nu_{\text{C-N}})$ ⁴. This band shifts to lower regions by as much as 100 cm⁻¹ in the complexes. It is likely that the metal ion coordinates through both the nitrogen atom of the hydrazonic residue and sulphur atom of the ligand.

In preliminary investigations, it was found that the complexes were partially oxidized by CAT at all pH but the rate of oxidation slowed down beyond pH 4 (solubility of complexes also decreased beyond this pH) and the reaction was found to be very fast and stoichiometric at pH 4. This behaviour could probably be attributed to the high rate of disproportionation of monochloramine-T present at this pH, to dichloramine-T and *p*-toluene sulphonamide, as suggested by Higuchi *et al.*⁶.

The following procedure is recommended for estimating the complexes.

To 25 cc of 0.1 N CAT in an iodine flask add aliquots of the complex (2 to 30 mg) prepared in acetate buffer of pH 4 and shake the contents. Set aside for 5 minutes, shaking occasionally. Rinse down with 20 ml of water, add 10 ml of 2 N H₂SO₄ and 10 ml of 20% KI solution and titrate with 0.1 N sodium thiosulphate. Run a blank with CAT solution alone.

The results of oxidation of the complexes are shown in Table I. It is evident that the ligand gets oxidised with 24 electron change according to the following stoichiometry:



Here M = Zn or Cd or Hg or Ni; X = SO₄ or (ClO₄)₂ or Cl₂ or (NO₃)₂.

It was found that the products of oxidation or the metallic ions at the concentrations employed did not react with the oxidant. But

the reaction was found to be sluggish with larger quantities of mercury complex. Investigations revealed that at higher concentrations mercuric chloride forms a white precipitate with CAT solution which slowly liberates iodine from KI solution. Also when the method was tried with some copper and cobalt complexes of TSC, the reactions were not stoichiometric, as these metallic ions were found to interfere seriously with the oxidation.

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in Chemistry,
Manasagangotri,
Mysore-6, India, October 8, 1971.

1. Mahadevappa, D. S. and Ananda Murthy, A. S., *Talanta*, 1970, **17**, 431.
2. Findlay, A., *Practical Physical Chemistry*, Longmans, London 1954 p 268.
3. Mashima, M., *Bull. Chem. Soc. Japan*, 1964, **36**, 974.
4. Burna, G. R., *Inorg. Chem.*, 1968, **7**, 277.
5. Campbell, M. J. and Grzeskowiak, R., *J. Chem. Soc., A*, 1967, p. 396.
6. Higuchi, T., Ikada, K. and Hussain, A., *Ibid.*, B, 1967, p. 546.

5-NITRO-PYRIMIDINES

5-NITRO-PYRIMIDINES have been claimed to possess antibacterial¹ and antiprotozoal² properties. Although syntheses of some of the corresponding 6-methyl derivatives have been reported in literature^{3,4} no reference has been made about their biological activity. Hence, the following work was undertaken and the compounds synthesised were screened for their anthelmintic, antibacterial and antiprotozoal properties. They were all inactive.