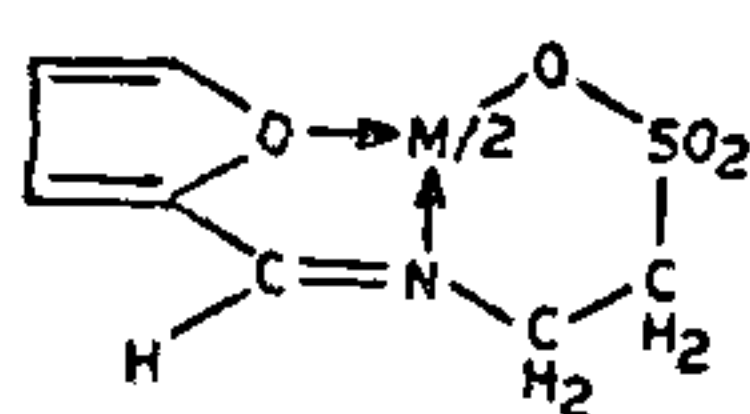


HFB-CHELATES



HFE-CHELATES

WHERE  $M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II)$  AND  $Cu(II)$

FIG 1 METAL CHELATES OF *o*-(*N*- $\alpha$ -FURFURALIDENE IMINO) BENZENE SULPHONIC ACID (HFB) AND *o*-(*N*- $\alpha$ -FURFURALIDENE IMINO) ETHANE SULPHONIC ACID (HFE).

The authors are thankful to U.G.C., New Delhi, for the award of fellowship to one of them (N. K. S.)

Department of Chemistry,  
University of Jodhpur,  
Jodhpur,  
February 13, 1978.

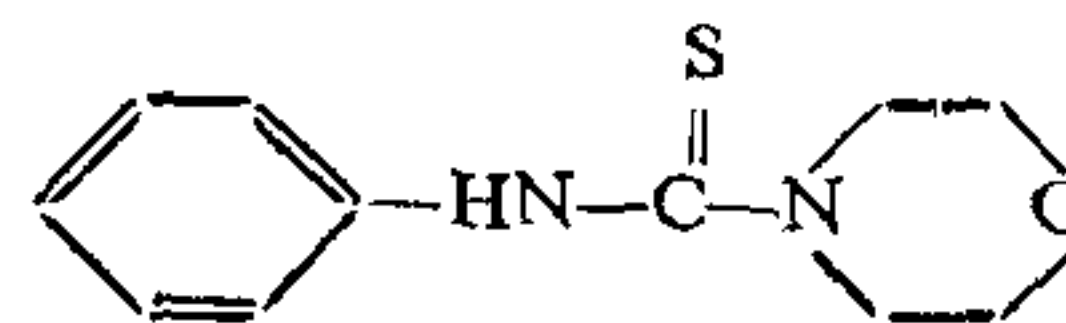
N. K. SANKHLA.  
C. P. GUPTA.  
R. K. MEHTA.

1. Cotton, F. A., *Prog. Inorg. Chem.*, 1966, 7, 88.
2. Hodgson, D. J., *Ibid.*, 1975.
3. Pfeiffer, P., Offermann, W. and Werner, H. J., *Prakt. Chem.*, 1942, 159, 313.
4. Yamada, S., Kuge, Y. and Yamanouchi, K., *Bull. Chem. Soc.*, 1967, 40, 1864.
5. Yamada, S., *Co-ordin. Chem. Review*, 19, 1, 415.
6. Figgis, B. N. and Nyholm, R. S., *J. Chem. Soc.*, 1958, p. 4190.
7. Mehta, R. K. and Gupta, R. K., *Indian J. Chem.*, 1973, 11, 56.

### COMPLEXES OF MORPHOLINE-4-THIOCARBONIC ACID ANILIDE WITH TELLURIUM(IV) AND TELLURIUM(II)

TETRAMETHYLTHIOUREA has been reported to form complexes with both  $Te(IV)^{1-3}$  and  $Te(II)^4$  whereas thiourea and its other substituted derivatives studied

have been shown to stabilise only  $Te(II)^5$ . While extending on the reported work<sup>6</sup> on complexation tendencies of morpholine-4-thiocarbonic acid anilide (MTA),



we found that this ligand interacted with  $Te(IV)$  in hydrochloric and hydrobromic acid media to yield  $TeCl_4 \cdot 2MTA$  (A) and  $TeBr_4 \cdot 2MTA$  (B), respectively and in hydroiodic acid medium to yield  $TeI_2 \cdot 2MTA$  (C). This is the only second example where a thio-urea is shown to form  $Te(IV)$  complexes.

Complexes A and B were prepared by treating 0.8 g (5 mM) of  $TeO_2$  dissolved in 7 ml conc. HCl/HBr with 2.2 g (10 mM) of MTA dissolved in 30 ml acetone. Both A and B were precipitated in near quantitative yield and were washed with dilute HCl/HBr and dried in vacuum. The complex C was precipitated slowly in 30 minutes on mixing solutions of 0.4 g (2.5 mM)  $TeO_2$  in 30 ml of 2M HI and of 3.3 g (15 mM) MTA in 30 ml acetone.†

The analytical data on the complexes is reported in Table I. The oxidation state of tellurium, in addition to being derived from elemental analysis, was also checked by treatment of the complexes in hydrohalic acid media with excess sodium diethyldithiocarbamate (Na DDTC) and testing by analysis whether the resulting dithiocarbamate preparations were  $Te^{IV}$  (DDTC)<sub>4</sub><sup>7</sup> or  $Te^{II}$  (DDTC)<sub>2</sub><sup>8</sup>. Iodide has been recently reported<sup>9</sup> to cause greater redox reactivity in complexes of tellurium with sulphur ligands and this is illustrated in the present work also. The complexes were indefinitely stable under non-humid conditions and were readily decomposed on contact with water, methanol and ethanol in absence of hydrohalic acids.

$TeCl_4 \cdot 2MTA$  and  $TeBr_4 \cdot 2MTA$  were nonconducting in dichloromethane solutions and osmometric studies (concentration range : 0.0003 M; solvent:

TABLE I

Compound	Colour	% composition					
		Te	X	C	H	N	S
$TeCl_4 \cdot 2MTA$ (A)	Yellow	17.60 (17.86)	19.61 (19.86)	37.10 (36.99)	3.90 (3.95)	7.50 (7.84)	9.20 (8.96)
$TeBr_4 \cdot 2MTA$ (B)	Orange	13.40 (14.31)	36.30 (35.83)	30.00 (29.62)	3.10 (3.16)	6.40 (6.28)	7.30 (7.19)
$TeI_2 \cdot 2MTA$ (C)	Red orange	15.71 (15.45)	31.40 (30.73)	31.80 (31.99)	3.36 (3.41)	6.69 (6.78)	7.83 (7.76)

X = halide; expected values in parenthesis.

TABLE II  
Infrared spectra (KBr) pellets) in  $\text{cm}^{-1}$  of complexes

Compound	N-H stretch	N-H bend and thioamide CN	C-S stretch	Ring C-N-C	Ring C-O-C
MTA ligand	3140m 3080m	1580m 1520s	700s	1150m	1110s
$\text{TeCl}_4 \cdot 2\text{MTA}$	3450m 3160m	1575m 1535m	690s	1145m	1100s
$\text{TeBr}_4 \cdot 2\text{MTA}$	3420m 3150m	1570m 1535m	690s	1145m	1110s
$\text{TeI}_2 \cdot 2\text{MTA}$	3450br 3160m	1580m 1530m	690s	1150m	1095s

dichloromethane) indicated molecular weights of 700 and 885 respectively for the two complexes. This showed that the complexes were monomeric in solution (expected; 714 and 892 respectively). No suitable solvent was available for  $\text{TeI}_2 \cdot 2\text{MTA}$ .

The infrared characteristics of the complexes are indicated in Table II.

In view of the poor ligation characteristics of the ethereal O and the thiureide N and the acknowledged soft basicity of thiureide S and the soft acidity of Te(II) and to a less extent of Te(IV), coordination of MTA to Te only through S is expected in the complexes although MTA has four possible coordination sites. In conformity with this expectation, the C-S stretch of the ligand does show a significant lowering in the complexes though not to an appreciable extent. Far i.r. results were collected but it was difficult to pick out the Te-S absorptions from the large number of bands observed in this region.

The electronic spectra of the complexes in dichloromethane ( $2-4 \times 10^{-5}$  M solutions) revealed mostly intraligand transitions at  $\nu$  44 kK ( $\phi \epsilon = 2.4 - 9.7 \times 10^4$  in  $\text{mol}^{-1} \text{cm}^2$ ), 38 kK ( $2.9 - 6.4 \times 10^4$ ) and 35 kK ( $1.6 - 3.6 \times 10^4$ ). In addition the chloro complex showed charge transfer absorption at 23.53 kK ( $1.03 \times 10^3$ ) and the bromo complex at 24.39 kK ( $6.18 \times 10^3$ ) and 23.26 kK ( $1.8 \times 10^3$ ).

Department of Chemistry,  
Indian Institute of  
Technology,  
Madras 600 036, India,  
May 2, 1978.

G. ARAVAMUDAN,  
CHHAYA JANAKIRAM.

1. Katarasos, N. and George, J. W., *J. Inorg. Nucl. Chem.*, 1969, 31 (11), 3505.
2. Husebye, S. and George, J. W., *Inorg. Chem.*, 1969, 8 (2), 313.

3. Esperas, S., George, J. W., Husebye, S. and Mikalsen, O., *Acta Chem. Scand.*, 1975, A29, 141.
4. Foss, O. and Hauge, S., *Ibid.*, 1959, 13, 2155.
5. —, *Selected Topics in Structural Chemistry*, Universitet forlaget, Oslo, 1967, p. 147.
6. Venkappayya, D. and Brown, D. H., *J. Inorg. Nucl. Chem.*, 1974, 36, 1023.
7. Husebye, S. and Svaeren, S. E., *Acta Chem. Scand.*, 1973, 27, 763.
8. Fabioni, C., Spagna, R., Vaciago, A. and Zambonelli, Z *Acta Cryst.*, 1971, B27, 1499.
9. Sethuraman, P. R., Udupa, M. R. and Aravamudan, G., *J. Inorg. Nucl. Chem.*, 1973, 35, 3291.

#### GRAVIMETRIC ESTIMATION OF Pd(II) WITH *o*-(2-PYRROLIDENEIMINO) BENZOIC ACID

SEVERAL gravimetric reagents<sup>1,2</sup> have been suggested for the estimation of Pd(II). The present note deals with the use of *o*-(2-pyrrolideneimino) benzoic acid ( $\text{H}_2\text{PB}$ ) as a gravimetric reagent for Pd(II) since the synthesis of the reagent is simple and the reagent highly specific. The Pd(II)-complex is insoluble in water and can thus form the basis of a quantitative separation procedure.

$\text{H}_2\text{PB}$  was prepared from pyrrole-2-carboxaldehyde and *o*-aminobenzoic acid by the method reported earlier<sup>3</sup>, m.p. 180°. It gives a lemon-yellow precipitate with Pd(II) in the pH range 0.7-3.2.

A stock solution of Pd(II) (0.6 g/l) in 0.1M HCl was standardised gravimetrically by the dimethyl glyoxime method<sup>4</sup>.

*Determination of Pd(II)*: An aliquot of the metal ion solution was diluted to about 150 ml, its pH was adjusted between 0.7-3.2 with HCl (1.0 N) and