

Synthesis and characterisation of 4-morpholinyl thiocarbonic acid amide (MTA) and its Cu(I) complex

JYOTSNA PANDEY

State Forensic Science Laboratory, Sagar (India).

(Received: March 10, 2009; Accepted: April 13, 2009)

ABSTRACT

4-Morpholinyl thiocarbonic acid amide synthesized and its Cu(I) complex was prepared. Both were characterized on the basis of elemental analysis, spectral studies, magnetic susceptibility measurement and amperometric titration. Analytical data indicate metal to ligand ratio 1:2. Infrared spectra showed the complexation through the S and N both. Magnetic measurement confirmed the diamagnetic behavior of the complex. An amperometric method for the estimation of Cu(I) with MTA further confirmed the MTA:Cu ratio 1:1. Experimental and calculated statistical data support the utility of the method for determination of Copper.

Key words: 4-morpholinyl thio carbonic acid amide, copper complex, spectral studies, amperometric titration.

INTRODUCTION

A number of complexes of substituted thiourea derivatives have been reported in the literature¹⁻⁸. Mostly in the complexes reported, coordination of the ligand was through sulphur atom. However, in a few cases^{2,9,10} nitrogen coordination has been reported.

The present work reports the analytical and spectral (IR) examination of Cu(I)- 4-morpholinyl thio carbonic acid amide (MTA) complex. Based on the MTA-Cu complexation and amperometric method, for the trace determination of copper has also been suggested.

EXPERIMENTAL

All the reagents used werw of Anala R/BDH grade

Preparation of 4-morpholinyl thio carbonic acid amide (MTA)

Ligand was prepared by the method of Henery and Dehn¹¹. Concentrated hydrochloric acid

(1ml.) was added to a suspension of morpholine (2.1 ml) with constant stirring and heated for 1-2 minutes from hydrochloride. 2.4 gm potassium thiocyanate and 10ml. of water was added to above solution and the resulting mixture was evaporated to dryness on water bath. The amide was separated from then potassium chloride by extraction with absolute ethyl alcohol. Partial evaporation of the alcohol and cooling gave crystals. Ligand was purified by recrystallisation with ethanol having m.pt. 150-152°C.

Preparation of 4-morpholinyl thio carbonic acid amide-Cu(I) complex

For the preparation of Copper (I) complex, initially Copper (II) salt was used which was reduced to copper (I) by substituted thiourea, the ligand¹². To the cold aqueous solution of copper (II) sulphate, aqueous solution of MTA was added with constant stirring. A thick pale white precipitate thus obtained was allowed to settle, then filtered, washed thoroughly with distilled water and dried in vacuum. Decomposes at 203°C found- C9:28.68), HJ: (4.79), N:(13.34), S:(15.29) & Cu: (30.30)%

Molecular formula $C_5H_{10}N_2OSCu$ require-C:9:28.65), H: (4.77), N: (13.36), S: (15.27), & Cu: (30.32)%

Amperometric Titration

For amperometric titration experimental sets of solutions containing varying amount of copper (II) in 0.5M potassium chloride were prepared. The pH of these solutions was adjusted to 5.25. The titrant 4-morpholinyl thio carbonic acid amide (MTA) solution was prepared and its pH was adjusted to 5.25.

Instrumentation IR Spectroscopy

The IR absorption spectra were recorded on Perkin-Elmer grating infrared spectroscopy model-157, in KBr pallets from the range 4000-650 cm^{-1} .

Amperometric titration-The amperometric titrations were performed on a manually operated polarograph with multi flex galvanometer (sensitivity 8.10×10^{-9} amp/div.). A d.m.e. was used as an indicator electrode and mercury pool as reference. The capillary used for d.m.e. had a m value of 2.3733 mg/sec. at a drop time 3.0sec., in air free 0.5 M potassium chloride at 35 cm effective height of mercury column. An Elico digital pH meter model (L 1-120) was used for pH measurements. All the measurements were made at room temperature $27^\circ C (\pm 0.5^\circ C)$.

The current voltage curve for MTA and copper were separately recorded in 0.5 M KCl at $pH = 5.258 \pm 0.02$. The titrations were performed at an applied voltage of 0.3 V vs Hg pool; the plateau potential of copper wave at which MTA is unaffected was fixed on a potentiometer for the purpose of amperometric titration.

RESULTS AND DISCUSSION

The structurally important IR spectral bands of the ligand and the corresponding bands in the complex are listed in Table 1.

In the region $3410-3200\ cm^{-1}$ three strong bands appear in the spectra of ligand 4-morpholinyl thio carbonic acid amide (MTA) which arise due to fundamental vibrations involving N-H stretching

Table 1: IR Data

Ligand/ Complex	ν (NH)	ν (CH)	(M-SCN)	δ (NH ₂)	Thio amide I	δ S(NH)+ ν (NCN)B	Thio amide II	Thio amide III	Morpho- line ring	H-N-C=S	Thio amide IV	S(NH)+ (NCN) A1+ (CS)	Out of plane (NH ₂)
MTA	3410s	2960		1620s	1500s	1460w	1370w	1050ms	1180ms	1270ms	930ms	1440ms 860ms 830s	690m
	3310s 3200s	2860 mbr					1310	100s	1120w 1100vs	1260w			660m
Cu:MTA	3400ms 3320vs 3200	2960m 2840m 2400	2100vs 2200m	1610vs	1540s	1450ms	1370s 1345s 1300ms	1065ms 1020m 100ms	1180m 1130w 1000vs	1290ms 1250m	920m 860ms 810ms 760ms	1435ms	670m 630m

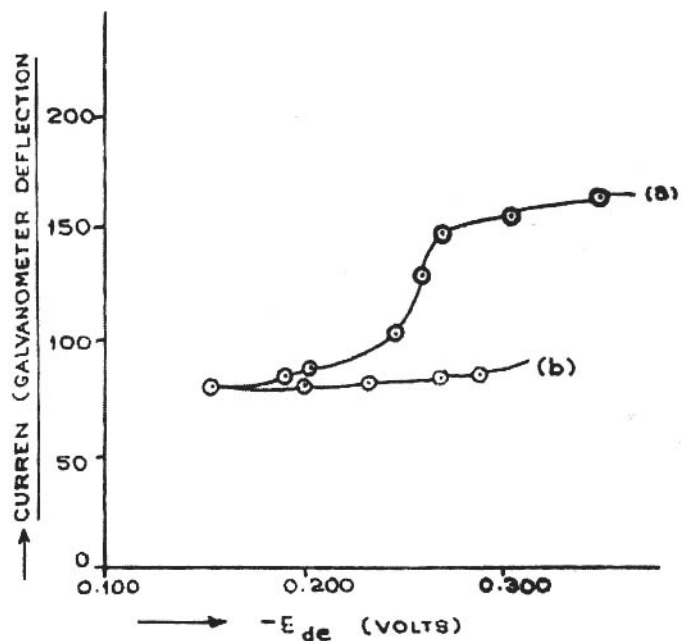


Fig. 1: Current voltage curves in 0.5 MKCl pH = 5.25 (B) 2mM Cu^+ and (b) 1mM MTA

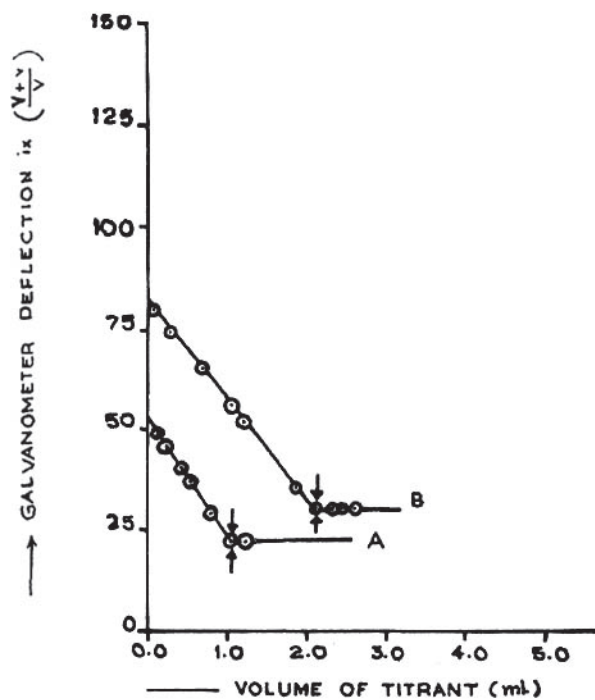


Fig. 2: Amperometric titration curves of $\text{Cu}(\text{I})$ with MTA. Concentration of $\text{Cu}(\text{I})$, (A) 0.01mM/10ml, (B) 0.02 mM/10ml. Conc of MTA - 0.01 mM/10ml

Table 2: Amperometric estimation of Cu(i) with MTA]

S. NO.	Amount of Cu taken	Amount of Cu fond	% error
1	0.0635	0.0636	+0.1%
2	0.1270	0.1270	-
3	0.3177	0.3177	-
4	0.6354	0.6354	-
5	0.9531	0.9532	-0.1%
6	1.2708	1.2708	-

modes¹³. Besides N-H stretching bands, comparatively weak bands appear near 2960-2880 cm^{-1} are due to stretching vibration corresponding to C-H bands, confirmation of aromatic character. One strong band observed near 1620 cm^{-1} can be attributed to NH₂ deformation vibration from 1620 cm^{-1} to 1610 cm^{-1} , supports metal to ligand coordination through nitrogen.

In the nitrogen containing thiocarbonyl derivatives three bands have been designated as "thioamide" (N-C=S) I, II and III, appear in the region 1395-1570 cm^{-1} , 1260-1420 cm^{-1} and 940-1140 cm^{-1} respectively¹⁴. The band around 1500 cm^{-1} in the spectra of ligand, which is assigned as thioamide I, is shifted towards higher side with no change in intensity. Thioamide II band of the ligand at 1370-1310 cm^{-1} is almost unaffected. Band near 1065-1000 cm^{-1} is of thioamide III and is spited in the complex. The band observed between 930-830 cm^{-1} , sometimes designated as thioamide IV involves mainly C=S stretching vibration. Lowered wave number of thioamide IV and diminished intesity of thioamide III and IV is indication of sulphur coordination.

Band near 1270-1260 cm^{-1} is of mixed H-N-C=S band due to C-N antisymmetric stretching and deformation motions. In complex it shifts from its original position by 20 cm^{-1} . A sharp band which appears at 2100 cm^{-1} is an indication of M-SCN type of bonding in the complex^{15,16}.

Bands at 1180-1100 cm^{-1} are due to ring (C-N-C) and (C-O-C) of morpholine. If coordination was to occur through the nitrogen or oxygen of morpholine ring, there should be a change in the

absorption due to (C-N-C) or (C-O-C) modes¹⁷. This was not observed in complex.

The band observed near 1460 cm^{-1} in the spectra of ligand (MTA) involves mainly NH₂ rocking motion with some contribution from C=S stretching and C-N asymmetric vibrations of B1 type. Another band which appear around 1440 cm^{-1} in the ligand spectra involves NH₂ deformation, A1 type NCN symmetric stretching and C=S stretching vibrations. In complex this band is slightly shifted towards lower frequency with almost no effect on intensity¹⁸.

Bands near 690-660 cm^{-1} are due to out of plane (NH₂) and are virtually unaffected on complexation.

In amperometric titration the current voltage behaviour of copper and MTA is 0.5 M potassium chloride (pH = 5.25 \pm 0.02) and ionic strength 0.5 adjusted with potassium chloride (Fig. 1), indicates a well defined cathodic reduction wave for copper (II). The height of diffusion is proportional to copper concentration.

On titrating each of the experimental set (containing varying amount of Cu(II) separately), at the voltage of 0.3V with MTA (pH=5.25 \pm 0.02), a white precipitate was obtained. The plot of galvanometer deflection, after necessary volume correction¹⁹ against the volume of MTA added, yielded 'L' shaped curve (Fig. 2). The end point indicated a metal to ligand ratio 1:1, which is in good agreement with observed analytical data already discussed in the present paper.

The data in Table – 2, clearly reveal the utility of this method for the trace determination of copper, with an error of less than \pm 0.1%.

Study of diverse ion effect

To study the diverse ion effect on the titration procedure discussed above, known amount of foreign ions viz., Na⁺ (23 mg), K⁺, NH₄⁺, Mg⁺⁺, Co⁺⁺, Cd⁺⁺, Zn⁺⁺, Pb⁺⁺, Cl⁻, Br⁻ and I⁻ 50 gm each where added to a definite amount of metal and this solution was titrated following the procedure by the presence of ions mentioned above. However, a small amount of Fe⁺⁺⁺, Ni⁺, Hg⁺⁺, Ag⁺, Au⁺, S⁻ interfered the titration procedure seriously.

REFERENCES

1. T. J. Lane, A. Yamaguchi, J. V. Cuagliano, J. A. Ratyan and S. Mizushima, *J. Am. Chem. Soc.*, **81**: 3824 (1959).
2. R. K. Gosavi and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, **29**: 1973 (1967).
3. A. D. Ahmed and P. K. Mandal, *J. Inorg. Nucl. Chem.*, **29**: 2344 (1967).
4. R. A. Bailey and T. R. Peterson, *Can J. Chem.*, **46**: 3119 (1968).
5. M. Nardelli and I. Chiesici, *Richerca Scient.*, **29**: 1733 (1959).
6. A. A. G. Tomliason, C. Bellitto and O. Piovesana, *J. Chem. Soc. (Dalton)*, 350 (1972).
7. O. Pivesana and C. Furlani, *J. Inorg. Nucl. Chem.*, **30**: 1249 (1968).
8. A. D. Ahmed and S. N. Bose, *J. Inorg. Nucl. Chem.*, **31**: 2883 (1969).
9. R. Rivest, *Can. J. Chem.*, **40**: 2234 (1962).
10. T. Tarantelli, P. Ricciesi and C. Furlani, *J. Inorg. Nucl. Chem.*, **31**: 3583 (1969).
11. Ronald A. Henry and William M. Dehn, *J. Am. Chem. Soc.*, **72**: 2806 (1950).
12. W. G. Palmer, *Experimental Inorganic Chemistry (Cambridge University Press)*, P. 132 (1965).
13. John R. Dyer, "Application of Absorption Spectroscopy of Organic Compounds", Prentice Hall of India Pvt. Ltd. Fourth printing, P. 36 (1978).
14. C. N. R. Rao and R. Venkataraghavan, *Spectr chim. Acta*, **18**: 541 (1962).
15. J. Chalt and L. A. Duncanson, *Nature*, **178**: 997 (1956).
16. J. Chalt and L. A. Duncanson, F. A. Hart and P. G. Oston, *Nature*, **181**: 43 (1958).
17. D. Venkappayya and D. H. Brown, *J. Inorg. Nucl. Chem.*, **36**: 1023 (1974).
18. R. K. Gosavi and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, **29**: 1937 (1967).
19. J. T. Stock, *Amperometric Titrations*, R. E. Kneger, *Pub. S. Huntington, New York* 7-8 (1975).