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Short Communication

Thermal, infrared and magnetic study of adducts of Cu(II) resacetophenone oximate complex with nitrogen bases

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Abstract

Some adducts of copper(II)-resacetophenone oximate complex with pyridine, α-picoline, β-picoline γ-picoline, piperidine and quinoline are prepared and their thermal, IR spectral and magnetic studies are carried out at room temperature. The data suggest that the adducts may have a binuclear structure.

Key words : Analytical reagent, binuclear structure, adduct formation.

1. Introduction

Extensive studies have been made using resacetophenone oxime (2, 4-dihydroxy acetophenone oxime) as an analytical reagent in these laboratories and elsewhere. Raju *et al*[1] reported that the oxime reacted with copper(II) giving an insoluble brown precipitate of composition 1 : 2 in acid medium.

Seshagiri and Rao[2] carried out the thermogravimetric study of the copper complex and reported that the complex is thermally stable up to 220° C. The copper complex is not extracted into hydrocarbon solvents. However, it was observed by Syamasundari[3] that the complex can be extracted into toluene in the presence of bases containing nitrogen. This has been ascribed by her to the adduct formation between the complex and the base. Adduct formation[4,5] is known to force bivalent metal ion such as Cu(II) to dimerise in its complexes, thus making the complex exhibit unusual magnetic moments. This type of magnetic exchange interactions of Cu(II) complexes have drawn much interest in recent years[6,7] even though the mechanism of exchange remains controversial. The most widely accepted interpretation is a direct metal-metal interaction[8–10], the magnitude being dependent on the metal-metal distance and the nature of the terminal ligand. These facts prompted the present authors to undertake the preparation and the study of infrared spectrophotometric, thermal and magnetic behaviour of nitrogen base adducts of copper (II) resacetophenone oximate complex. The present communication describes the results obtained in the studies on the adducts with pyridine, picolines, piperidine and quinoline.

2. Experimental

2.1. *Chemicals*

All the chemicals used are of AnalaR grade and the bases are purified by the recommended procedure[11].

2.2. *Preparation of the adducts*

The oximate complex of copper is prepared by the procedure of Raju *et al*[1]. The complex is dissolved in slight excess of freshly purified base and the excess of base is slowly volatilised at temperature not exceeding 100° C. The solid obtained is used for the studies.

2.3. *Thermogravimetric measurements*

Thermograms are recorded in the presence of air using Stanton Model 5M Recording unit. The heating rate is maintained at 6°/minute. The data are presented in Table I.

2.4. *IR spectra*

The IR spectra in KBr are recorded in the region 4000–600 cm^{-1} with the Perkin-Elmer 257 instrument. The important spectral data are presented in Table II.

2.5. *Magnetic susceptibility measurements*

Magnetic susceptibility measurements are made over solid specimens using Guoy method at room temperature. The Guoy tube is calibrated employing $HgCo(NCS)_4$. Diamagnetic corrections for ligand atom and ions are made using Pascal's[12] constants, Magnetic moments are presented in Table II.

3. Results and discussion

3.1. *Thermogravimetric studies*

Thermograms show that the first decomposition of the adducts started at 110° C except in the case of piperidine adduct and continued up to 150–160° C. In the temperature range c.a. 150 to 210° C the residue obtained in the first decomposition is stable. This is followed by a loss in weight at constant temperature at about 210° C. The final

Table I

Thermogravimetric data

Probable composition of the dimer	Decomposition range (° C)	% loss in weight		Probable component lost
		Found	Calculated	
$Cu_2(RPO)_4(py)_2$	110–160	15·00	16·54	Two molecules of pyridine
	210–360	67·00	70·15	Four molecules of the oxime
$Cu_2(RPO)_4(\alpha\text{-pic})_2$	100–140	14·00	18·90	Two molecules of α-picoline
	220–370	66·00	68·16	Four molecules of the oxime
$Cu_2(RPO)_4(\beta\text{-pic})_2$	100–200	18·00	18·90	Two molecules of β-picoline
	220–340	62·00	68·16	Four molecules of the oxime
$Cu_2(RPO)_4(\gamma\text{-pic})_2$	100–140	18·00	18·90	Two molecules of γ-picoline
	220–340	62·00	68·16	Four molecules of the oxime
$Cu_2(RPO)_4(pipy)_4$	80–120	27·00	27·30	Four molecules of piperidine
	180–340	55·00	61·79	Four molecules of the oxime
$Cu_2(RPO)_4(Quin)_2$	110–160	23·00	24·46	Two molecules of quinoline
	210–360	60·00	63·39	Four molecules of the oxime

Table II

Infrared and magnetic moment data

Compound	OH	ν cm^{-1} C=N	N—O	μ_{eff} (BM)	*pKa* of the base
$Cu(RPO)_2$	3220	1590	940	1·80	—
$Cu_2(RPO)_4(pipy)_4$	3240	1575	825	1·47	11·20
$Cu_2(RPO)_4(Quin)_2$	3200	1580	825	1·10	4·80
$Cu_2(RPO)_4(py)_2$	3200	1575	940	1·60	5·25
$Cu_2(RPO)_4(\alpha\text{-pic})_2$	3200	1580	830	1·50	5·97
$Cu_2(RPO)_4(\beta\text{-pic})_2$	3400	1580	830	1·43	5·68
$Cu_2(RPO)_4(\gamma\text{-pic})_2$	3400	1580	800	1·00	6·02

decomposition involving the change of temperature took place up to c.a. 360° C. The weight losses corresponding to different decompositions mentioned above and the probable component lost are presented in Table I. The final product of decomposition above 360° C corresponds to metallic state in each case.

3.2. *IR spectral studies*

A comparison of the spectral data (cf. Table II) of the complex and the adducts shows that the C=N, and N—O frequencies are lowered in the case of adducts. The magnitude of the lowering in the frequency of C=N is very much less compared to that observed in N—O frequency. It is noticed that γ-picoline exerted a greater lowering in the case of unhydrogenated bases studied. The shift in N—O frequency showed a linear relationship with *pKa* values (cf. Table II) of the base except in the case of α-picoline and quinoline. Similar trend is noticed by W. E. Marsh *et al*[13] with $-2J$ values of copper(II) propionate adducts. The deviation in the case of α-picoline and quinoline can be traced to steric factors. The larger shift in the case of piperidine is also obvious from its large *pKa* value (11·2).

3.3. *Magnetic studies*

All the adducts are found paramagnetic and the magnetic moment values are less than the spin only value of 1·73 BM of copper and also than the 1·8 BM obtained for the copper complex. This decrease can be ascribed to the magnetic exchange interaction, the exchange being due to the direct metal-metal interaction. These interactions mentioned earlier are dependent on the nature of the terminal ligand and is larger as the ligand supplies more electron density to the metal ion. The following order is noticed in the interaction :

$$\gamma\text{-}pic > \alpha\text{-}pic \simeq \beta\text{-}pic > py.$$

The order is in accordance with the electron donating ability of the terminal ligand. A linear relation between the magnetic moment and the *pKa* of the ligand is obtained except in the case of α-picoline for the reasons mentioned earlier. Adduct formation may result in the formation of a penta co-ordinated complex or a binuclear complex. However, no change is expected in the magnetic behaviour of the adduct if it is a mere change of co-ordination number from 4 to 5. The authors, therefore, propose that the adducts under study may have binuclear structures. Similar observation was reported by Borel *et al*[14, 15] in their studies on the adducts of Cu(II)-propionate with α-picoline and β-picoline.

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References

1. RAJU, N. A. AND NEELAKANTAM, K. *Curr. Sci.*, 1958, **19**, 383.
2. SESHAGIRI, V. AND RAO, S. B. *Z. Anal. Chem.*, 1972, **262**, 275.
3. SYAMASUNDARI DEVI, V. S. D. *M.Phil. Dissertation*, SVU Autonomous Post-Graduate Centre, Anantapur, 1978.
4. KATO, M., JONASSEN, H. B. AND FUNNING, J. C. *Chem. Rev.*, 1964, **64**, 99.
5. OLDHAM, C. *Progr. Inorg. Chem.*, 1968, **10**, 223.
6. HATFIELD, W. E. AND WYMAN, R. *Transition Metal Chem.*, 1969, **5**, 47.
7. JOTHAM, R. W., KETTLE, S. F. A. AND MARKS, J. A. *J. Chem. Soc. (Dalton Trans.)*, 1972, p. 428.
8. FIGGIS, B. N. AND MARTIN, R. L. *J. Chem. Soc.*, 1956, Part **III**, p. 3837.
9. MARTIN, R. L. *New Pathways in Inorganic Chemistry*, University Press, Cambridge, 1968, pp. 175–231.
10. JOTHAM, R. W. AND KETTLE, S. F. A. *Chem. Comm.*, 1969, p. 258.
11. WEISSBERGER, A., PROSKAUER, E. S., RIDDICK, J. A. AND TOOPS, E. E. In *Organic Solvents*, 2nd edition, Ed. A. Weissberger, Interscience Publishers, New York, 1955.
12. SELWOOD, P. W. *Magneto Chemistry*, Interscience, New York, 1956, pp. 78 and 91.
13. MARSH, W. E., CARLISLE, G. O. AND HANSON, M. V. *J. Inorg. Nucl. Chem.*, 1977, **39**, 1839–1841.
14. BOREL, M. M., BUSNOT, A. AND LECLAIRE, A. *J. Inorg. Nucl. Chem.*, 1976, **38**, 1557.
15. BOREL, M. M., BUSNOT, A. AND LECLAIRE, A. *J. Inorg. Nucl. Chem.*, 1976, **38**, 235.