

CCA-1663

YU ISSN 0011-1643

UDC 546.56

Note

Magnetic and Spectral Properties of 2-Methylbenzoxazole, Benzothiazole, and 2-Methylbenzothiazole Complexes with Copper(II) Dichloroacetate

Ahmed A. Mohamed,^a Aref A. M. Aly,^b and Mohamed El-Shabasy^c

Chemistry Department, ^aQena University, Qena, Egypt, ^bAssiut University, Assiut, Egypt, ^cPhysics Department Minia University, Minia, Egypt

Received May 10, 1985

The complexes in the title have been synthesized and their magnetic and spectral behaviour have been studied. Magnetic susceptibility was determined in the temperature range of 80—300 K. The IR spectra were obtained in KBr pellets, and UV spectra in acetone. The conductivity of the complexes in acetone solutions were also measured.

INTRODUCTION

Haloacetate ions form a great number of complexes with transition metal ions giving rise to different coordination number and stereochemistry. In these complexes they can act as monodentate, bidentate (chelating or bridging) acetate groups.¹⁻⁴ Oxazole and thiazole rings play an important role in biological systems *e. g.* as a regulator for plant growth.^{5,6} We have therefore prepared the bis complexes of copper dichloroacetate with 2-methylbenzoxazole, (2-mBoz), benzothiazole, (Btz), and 2-methylbenzothiazole, (2-mBtz), and studied their magnetic and spectral behaviour.

EXPERIMENTAL

All chemicals were of analytical grade. Bis(dichloroacetato)copper(II) was prepared in solution.¹⁰ The azole ligands were prepared according to literature procedures.^{5,12}

Bis(dichloroacetato)bis(2-methylbenzoxazole)copper(II)

A solution of an excess amount (25 mmol) of the ligand in ethanol (20 mL) was added to an ethanolic solution (20 mL) of $\text{Cu}(\text{Cl}_2\text{ac})_2$ (10 mmol). The mixture had been allowed to stand for some days, and the separated green crystals were then collected, washed with ethanol and dried *in vacuo* over P_2O_5 . m. p. 170 °C; yield 85%.

Found: C 40.79, H 2.80, N 4.71, Cl 24.13, Cu 10.78%.

Calcd.: C 41.02, H 2.75, N 4.78, Cl 24.21, Cu 10.84%.

Bis(dichloroacetato)bis(benzothiazole)copper(II)

This was prepared similarly to the 2-methylbenzoxazole complex. Bluish green crystals. m. p. 110 °C (decomp.); yield 70%.

Found: C 36.60, H 2.11, N 4.69, Cl 24.10, Cu 10.65%.

Calcd.: C 36.66, H 2.05, N 4.74, Cl 24.04, Cu 10.77%.

Bis(dichloroacetato)bis(2-methylbenzothiazole)copper(II)

The preparation of this complex followed essentially the same procedure as for the 2-methylbenzoxazole complex. Green crystals. m. p. 180 °C (decomp.); yield 75%.

Found: C 38.81, H 2.74, N 4.48, Cl 22.86, Cu 10.19%

Calcd.: C 38.89, H 2.61, N 4.53, Cl 22.95, Cu 10.28%.

Physical measurements. Magnetic susceptibility in the temperature range of 80—300 K was determined by the Gouy method. Molar susceptibilities were corrected for diamagnetism of the constituent elements using Pascal's constants. The IR spectra (4000—200 cm^{-1}) were obtained with potassium bromide pellets using a Perkin-Elmer 599 B recording spectrophotometer. Electronic spectra in acetone solutions were obtained with a Shimadzu UV-200 S and matched 1.0 cm quartz cells. The conductivity of the complexes in acetone solutions was measured with LF Digi 550 conductance bridge at 25 °C.

RESULTS AND DISCUSSION

The complexes are green, stable in air and soluble in most of the common organic solvents. The infrared data are given in Table I. The magnetic behaviour and the values for magnetic moments of $\text{Cu}(\text{Cl}_2\text{ac})_2(2\text{-mBoz})_2$ and $\text{Cu}(\text{Cl}_2\text{ac})_2(2\text{-mBtz})_2$ indicate that these two complexes are associated in the solid state.^{7,8,9} This is in accord with the tendency of the haloacetate anion to form such associated complexes.¹⁰

The values of magnetic moments $\mu_{\text{eff}}/\mu_{\text{B}}$ at 300 K: 1.46 (I), 1.84 (II), 1.71 (III) together with the IR data (discussed below) are most likely consistent

TABLE I
Pertinent IR Bands (ν/cm^{-1}) of the Complexes

Complex	Assignment		
	ν asymm. CO_2^- cm^{-1}	ν symm. CO_2^- cm^{-1}	Δ cm^{-1}
1 — $\text{Cu}(\text{Cl}_2\text{ac})_2(2\text{-mBoz})_2$	1695	1410	285
2 — $\text{Cu}(\text{Cl}_2\text{ac})_2(\text{Btz})_2$	1610, 1630	1390, 1410	220, 220
3 — $\text{Cu}(\text{Cl}_2\text{ac})_2(2\text{-mBtz})_2$	1690	1410	280

with a monomeric structure of $\text{Cu}(\text{Cl}_2\text{ac})_2(\text{Btz})_2$ with a bidentate haloacetate group. The three complexes obey the Curie-Weiss law and the values of Θ are the following: 38 K (I), —30 K (II) and 8 K (III).

The difference between asymmetric and symmetric C—O stretching frequencies (Δ) in the IR spectra is larger for $\text{Cu}(\text{Cl}_2\text{ac})_2(2\text{-mBoz})_2$ and $\text{Cu}(\text{Cl}_2\text{ac})_2(2\text{-mBtz})_2$ than that of $\text{Cu}(\text{Cl}_2\text{ac})_2(\text{Btz})_2$. A bridging acetate group in the first two complexes and a bidentate group in the latter complex^{3,10} can thus be assumed. Bands that appear in the regions 260—280 cm^{-1} and 320—360 cm^{-1} are assigned to ν (Cu—O) and ν (Cu—N) respectively. A number of bands, which are shown in the region 2990—3010 cm^{-1} are ascribed to ν CH-stretching of the methyl groups and the phenylrings in the ligands. The three complexes exhibit

the C—Cl stretching frequency as a rather intense band in the 750 cm^{-1} region.

The electronic spectra of the complexes show one broad absorption band in acetone solutions centered at about 13000 cm^{-1} for $\text{Cu}(\text{Cl}_2\text{ac})_2(2\text{-mBoz})_2$ and $\text{Cu}(\text{Cl}_2\text{ca})_2(2\text{-mBtz})_2$ and at about 16000 cm^{-1} for $\text{Cu}(\text{Cl}_2\text{ac})_2(\text{Btz})_2$, which is assigned to the d-d transition. This band occurs at lower frequency for the first two complexes compared with that of the last compound. This is probably due to an increase in steric hinderence in the methyl derivatives, which may cause the bond Cu—N to be longer and consequently lowering of the 10 Dq values. Further, the band position is similar to that of the band exhibited by analogous imidazole copper complexes.¹¹ This may indicate coordination of the azoles in the present complexes through nitrogen atoms, supporting the previous assignment of the IR-band in the region $320\text{--}360\text{ cm}^{-1}$ as $\nu\text{Cu—N}$. A further confirmation of this coordination site in these complexes comes from a study by Y. Muto *et al.*⁴ on a series of complexes of the general formula $\text{Cu}(\text{ac})_2 \cdot \text{L}$ (where L represents some azole derivatives). It was reported that in this series the nitrogen atom in the ligand L is most probably the donor atom.

The electronic spectra of the three prepared complexes have, in addition, an intense band in the range $29410\text{--}30760\text{ cm}^{-1}$, which can be assigned as a charge transfer band. Bands that appear in the range $40000\text{--}43000\text{ cm}^{-1}$ may be correlated with $\pi\text{--}\pi^*$ transitions.

The Nujol mull spectra of the complexes are more or less different from the solution spectra and the bands are much broader. It would appear that the stereochemistry around the Cu atom in the solid state is not similar to that of the solution.

Indeed, it is difficult (on the basis of the above magnetic and spectral data) to decide upon between a square planar and octahedral structure for the complexes.

REFERENCES

1. C. A. Agamber and K. G. Orrell, *J. Chem. Soc. (A)* (1969) 897.
2. A. V. Ablov, V. V. Gausilov, L. N. Molkova, L. N. Kumankou, and Yu. V. Yablokov, *Akad. Nauk., S.S.S.R., In Khim.* 6 (1969) 1501.
3. C. D. Rao, B. Paul, B. K. Mohapatra, and S. Guru, *J. Inorg. Nucl. Chem.* 40 (1978) 134.
4. Y. Muto, T. Tokii, K. Chijiwa, and M. Kato, *Bull. Chem. Soc. Jpn.* 57 (1984) 1011.
5. R. C. Elderfield, *Heterocyclic compounds* 5, John, Wiley & Sons., Inc. (1957).
6. L. S. Goodman and A. Gilman, *The Pharmacological Basis of Therapeutics*, MacMillan, Toronto (1971).
7. K. S. Patel and B. B. Adeleke, *Inorg. Nucl. Chem. Lett.* 16 (1980) 57.
8. K. S. Patel and J. O. Ikekwere, *J. Inorg. Nucl. Chem.* 43 (1981) 51.
9. J. Lewis, F. E. Mabbs, L. K. Royston, and W. R. Smail, *J. Chem. Soc. (A)* (1969) 291.
10. A. B. P. Lever and D. Ogden, *J. Chem. Soc. (A)* (1967) 2041.
11. S. V. Deshpande and T. S. Srivastava, *Polyhedron* 2 (1983) 761.
12. W. Theilacker, *J. Prakt. Chem.* 153 (1939) 54.

SAŽETAK**Magnetska i neka spektrometrijska svojstva 2-metilbenzoksazol-, benzotiazol- i 2-metilbenzotiazol-kompleksa sa bakar(II)-dikloroacetatom**

A. A. Mohamed, A. A. M. Aly i M. El-Shabasy

Sintetizirani su kompleksi navedeni u naslovu i ispitana su njihova magnetska i neka spektrometrijska svojstva. Magnetska svojstva ispitana su u temperaturnom području od 80—300 K, IR spektri snimljeni su u KBr, a UV spektri u acetonu. Ispitana je također i vodljivost acetonskih otopina navedenih kompleksa.