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PREPARATION AND MOLECULAR STRUCTURE OF BIS (TETRAMETHYLETHYLENEDIAMINE) COPPER(I) DICHLORO CUPRATE(I), [Cu (TMEDA)$_2$] [CuCl$_2$]

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Abstract

A complex of N, N, N', N', -tetramethylated ethylenediamine, TMEDA, with CuCl is prepared. The crystal and molecular structure of this complex is characterized by a single-crystal X-ray diffraction study. The complex is found to contain [Cu (TMEDA)$_2$]$^+$ cation which is nearly tetrahedral and the [CuCl$_2$]$^-$ anion is linear which Cu lies on a center of symmetry. Crystals are monoclinic space group $P2_1/n$ with four molecules/ unit cell of dimensions a = 9.240 (4), b = 14.930 (3), c = 14.288 (5) Å and ß = 97.02 (3)°. The final R value is 0.045 for 3808 reflections measured.

Introduction

The most frequently encountered copper(I) geometry is tetrahedral (four coordination number), though linear (two coordination number) and trigonal planar (three coordination number) structures are known. Some Cu(I) polymeric and cluster complexes exhibit higher coordination numbers [1-8].

Copper(I) chloride is the best starting material for the preparation of most Cu(I) complexes. In some cases such as Cu(I) amido complexes, CuCl disproportionates to Cu (0) and CuCl$_2$. Therefore, the best candidate for the preparation of these complexes is CuCl in the presence of N, N, N', N' - tetramethylethylenediamine.

In this research project, a complex of N, N, N', N', -tetramethylated ethylenediamine, TMEDA, with CuCl is prepared and investigated by a single-crystal X-ray diffraction.

Keywords: Preparation; Molecular structure; [Cu (TMEDA)$_2$] [CuCl$_2$]

Experimental Section

Preparation

Owing to the air sensitivity of the complex, all operations were carried out under a dry, oxygen-free, nitrogen atmosphere using standard Schlenk techniques. The solvent and N, N, N', N'-tetramethylethylenediamine were dried and distilled by standard methods before using.

The complex was prepared by the reaction of tetramethylethylenediamine in THF solution with CuCl. A 0.10 mole of CuCl was suspended in THF (100 ml) solution containing 0.10 mole TMEDA under nitrogen atmosphere. After a few minutes of stirring at boiling point of THF, the clear colorless solution was obtained. By cooling down the hot solution very slowly, large white crystals were formed which were suitable for X-ray crystallographic studies. The product was then identified by single-crystal X-ray diffraction.

Data Collection

A white octahedron crystal of $C_{12}H_{32}Cu_2Cl_2N_4$ having approximate dimensions of 0.500 X 0.500 X 0.500 mm was mounted on a glass fiber. All measurements were

made on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation and a 12kW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 20 carefully centered reflections in the range $30.12 < 2\theta < 40.02°$, corresponded to a monoclinic cell with dimensions:

a = 9.240 (4)Å
b = 14.930 (3)Å ß = 97.02 (3)°
c = 14.288 (5)Å
V =1956 (1) Å^3

For z = 4 and F.W. = 430.41, the calculated density is 1.461 g/cm^3. Based on the successful solution and refinement of the structure, the space group was determined to be:

$P2_1/n$ (#14) [9]

The data were collected at a temperature of -160 ± 1°C using the ω -2θ scan technique to a maximum 2θ value of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.30° with a take-off angle of 6.0°. Scans of (1.10 + 0.30 tan θ)° were made at a speed of 4.0°/ min (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

Data Reduction

Of the 3808 reflections which were collected, 3575 were unique (R_{int} = .083). The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo Kα is 24.5 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.40026E-06).

Structure Solution and Refinement

The structure was solved by direct methods [10]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement [11] was based on 2446 observed reflections ($I > 2.50\sigma(I)$) and 185 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \mid |Fo| - |Fc| \mid / \Sigma |Fo| = 0.045$$
$$R_w = [(\Sigma w (|Fo| - |Fc|)^2 / \Sigma w Fo^2)]^{1/2} = 0.049$$

The standard deviation of an observation of unit weight was 1.74 [12]. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. Plots of $\Sigma w (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/ λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.64 and –0.71 e$^-$ / Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber [9]. Anomalous dispersion effects were included in Fcalc [13] the values for Δf' and Δf" were those of Cromer [14]. All calculations were performed using the TEXSAN [15] crystallographic software package of Molecular Structure Corporation.

Results and Discussion

The crystals consist of $[Cu(TMEDA)_2]$ $[CuCl_2]$ complexes. The cation ion, $[Cu(TMEDA)_2]^+$, is nearly tetrahedral (see Figures I and II) and the anion ion, $[CuCl_2]^-$, is linear which Cu atom lies on a center of symmetry. The Cu atom in cation has a coordination number of four involving four donor atoms of the tetramethylethylenediamine, TMEDA, ligands. The Cu-N distances in the cation range from 2.132 (5) Å to 2.149 (4) Å, with an average of 2.140 Å. The Cu-Cl distances in anion are the same because of symmetry. Crystals are monoclinic space group $P2_1/n$ with four molecules per unit cell. The final R value is 0.045 for 3808 reflections measured. The final positional parameters, the thermal parameters for non-hydrogen atoms, the hydrogen atom parameters and distances, the figure ORTEP of the anion, the observed and calculated structure amplitude are available. The complex is diamagnetic, air and moisture sensitive, and white in color which is not surprising for Cu(I) complexes.

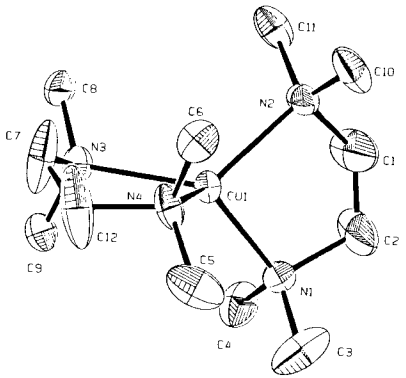

Figure I. ORTEP of the $[Cu(TMEDA)_2]^+$ cation showing the atomic numbering and thermal ellipsoids

Selected Bond Distances and Angles:

Cu(1)–N(1) = 2.134(5) Å	Cu(1)–N(2) = 2.149(4) Å
Cu(1)–N(3) = 2.134(4) Å	Cu(1)–N(4) = 2.132(5) Å
N(1)–Cu(1)–N(2) = 86.3(2)°	N(3)–Cu(1)-N(4) = 86.0(2)°
N(1)–Cu(1)–N(3) = 121.8(2)°	N(2)–Cu(1)–N(3) = 121.5(2)°
N(1)–Cu(1)–N(4) = 121.7(2)°	N(2)–Cu(1)–N(4) = 123.9(2)°

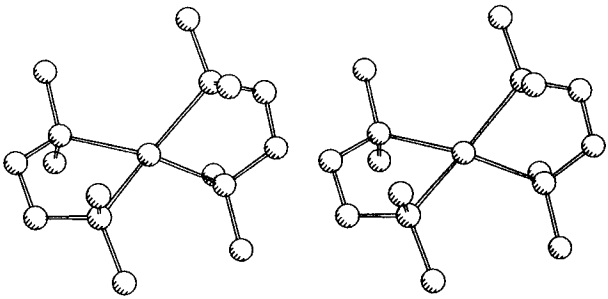

Figure II. ORTEP stereoview of the $[Cu(TMEDA)_2]^+$ cation

References

1. Engelhardt, L. M., Pakawatchai, C. and White, A. H. *J. Chem. Soc. Dalton Trans.*, 125, (1985).
2. Rath, N. P. and Holt, E. M. *J. Chem. Soc. Commun.*, 311, (1986).
3. Dyason, J. C., Engelhardt, L.M., Healy, P. C., Pakawatchai, C. and White, A.H. *Inorg. Chem.* **24**, 1950, (1985).

4. Dyason, J.C., Healy, P. C., Pakawatchai, C., Patrick, V. A. and White, A. H. *Ibid.* **24**, 1957, (1985).
5. Bowmakers, G. A., Clark, G. R. and Rogers, D. A. *J. Chem. Soc. Dalton. Trans.* 37. (1984).
6. Munakata, M., Kitagawa, S., Shimono, H. and Masuda, H. *Inorg. Chem.* **30**, 2610 (1991).
7. Mohr, B., Brooks, E. E., Rath, N. and Deutsch, E. *Ibid.* **30**, 4541, (1991).
8. Nickel, T., Pörschke, K. R., Goddard, R. and Krüger, C. *Ibid.* **31**, 4428 (1992).
9. Cromer, D. T. and Waber, J. T. *International tables for x-ray crystallography*. Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
10. Structure Solution Methods:
PHASE
Calbrese, J.C.; PHASE - Patterson Heavy Atom Solution Extractor. Univ. of Wisconsin-Madison, Ph.D. Thesis (1972).
DIRDIF
Beurskens, P. T.; DIRDIF: Direct methods for difference structures - an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.
11. Least-Squares:
Function minimized: $\Sigma w (|Fo| - |Fc|)^2$
where: $w = 4Fo^2 / \sigma^2 (Fo^2)$
$\sigma^2 (Fo^2) = [S^2 (C + R^2 B) + (pFo^2)^2]/ Lp^2$
S = Scan rate
C = Total integrated peak count
R = Ratio of scan time to background counting time
B = Total background count
Lp = Lorentz - polarization factor
p = p-factor
12. Standard deviation of an observation of unit weight:
$[\Sigma w (|Fo| - |Fc|)^2 / (No - Nv)]^{1/2}$
where: No = number of observations
Nv = number of variables
13. Ibers, J. A. and Hamilton, W. C. *Acta Crystallogr.*, **17**, 781 (1964).
14. Cromer, D. T. *International tables for x-ray crystallography*. Vol. IV, The Kynoch Press, Birmingham, England, Table 2. 3. 1 (1974).
15. TEXSAN – TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).