Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 97331, U.S.A.

Copper(II) Acetate Complexes of Bicyclic Tertiary Amines

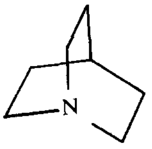
E. D. Stevens and J. T. Yoke[1]

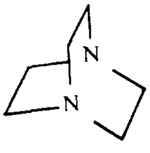
Received December 28, 1969

Triethylamine and N,N,N',N'-tetramethylethylenediamine (TMEN) are contrasted sterically with their bicyclic analogues, quinuclidine (QUIN) and triethylenediamine (TEDA) as ligands for copper(II) acetate in dimethylformamide (DMF). The complexes $[Cu(C_2H_3O_2)_2 \cdot TMEN]$, $[Cu(C_2H_3O_2)_2 \cdot DMF]_2$, $[Cu(C_2H_3O_2)_2 \cdot QUIN]_2$, *and* $[Cu(C_2H_3O_2)_2 \cdot 1/2TEDA]_2$ *have been prepared. Spectroscopic and magnetic data indicate that the TMEN complex does not have, and the other complexes do have, the type of dimeric structure known for copper(II) acetate hydrate.*

Introduction

Triethylamine and N,N,N',N'-tetramethylethylenediamine (TMEN) have recently been compared with their less sterically hindered bicyclic analogues quinuclidine (QUIN) and 1,4-diazabicyclo-[2.2.2.] octane or triethylenediamine (TEDA) as ligands toward silver nitrate[2] and copper(II) and cobalt(II chloride.[3]


QUIN


TEDA

A study of the cordination of these ligands to copper(II) acetate is now reported. It was of particular interest to attempt the preparation and magnetic characterization of amine complexes of the type $[Cu(C_2H_3O_2)_2 \cdot L]_2$ (L=amine or 1/2 diamine).[4] While such complexes with pyridine bases have been described,[5] the known complexes with aliphatic amines are generally of the type $[Cu(C_2H_3O_2)_2 \cdot 2L]$).[6] Copper acetate and laurate complexes of the formula $Cu(OOCR)_2 \cdot 1/2$ TEDA have been prepared, but not characterized.[7]

Experimental Section

Materials. The sources and purification of the amines have been indicated previously.[2] Dimethylformamide (DMF) and anhydrous ether were Analytical Reagent Grade. Copper(II) acetate monohydrate was prepared from Reagent Grade copper(II) nitrate hydrate by the method of Brauer.[8] *Anal.* Calcd. for $Cu(C_2H_3O_2)_2 \cdot H_2O$: Cu, 31.82. Found: 31.45.

Preparation of Complexes. The volume of a solution of 20 g copper(II) acetate monohydrate in 400 ml DMF at 50° was decreased to one-half at reduced pressure using a rotary evaporator. Blue-green crystals of $Cu(C_2H_3O_2)_2 \cdot DMF$ were formed on cooling the solution. The product was filtered, washed with DMF and hexane at 0°, and dried *in vacuo* over phosphorus(V) oxide. *Anal.* Calcd. for $CuC_7H_{13}NO_5$: Cu, 24.94; C, 33.00; H, 5.14. Found: Cu, 24.98; C, 32.63; H, 4.99.[9]

TMEN was added with vigorous stirring to a solution such as described above, until the mole ratio of diamine: copper slightly exceeded 1.0. The same procedure was followed, and royal blue crystals of $Cu(C_2H_3O_2)_2 \cdot TMEN$ were obtained, washed, and dried as above. *Anal.* Calcd. for $CuC_{10}H_{22}N_2O_4$: Cu, 21.34; C, 40.33; H, 7.45. Found: Cu, 21.29; C, 40.55; H, 7.48.

When the same method was followed using a mole ratio of TMEN: copper of 0.50, or using triethylamine (and also diethyl-, *n*-propyl-, and mono-, di, and tri-*n*-butylamines), products were obtained whose analyses corresponded approximately to that of the DMF complex.

Complexes of the bicyclic amines were made following the general procedure of Tennenhouse.[7] TEDA in a small amount of DMF was added to a solution of 5 g copper(II) acetate monohydrate in 250 ml DMF until the mole ratio of diamine: copper slightly exceeded 0.5. A light green precipitate of $Cu(C_2H_3O_2)_2 \cdot 1/2TEDA$ was formed. This was filtered, washed with DMF and ether, and dried *in vacuo* over sodium hydroxide. *Anal.* Calcd. for $CuC_7H_{12}NO_4$: Cu, 26.73; C, 35.37; H, 5.05. Found: Cu, 26.94; C, 35.37; H, 5.18. The light green complex $Cu(C_2H_3O_2)_2 \cdot QUIN$ was prepared in the

---

[1] To whom inquiries should be addressed.
[2] H. M. Hilliard and J. T. Yoke, *Inorg. Chem.*, *5*, 57 (1966).
[3] H. M. Hilliard, D. D. Axtell, M. M. Gilbert, and J. T. Yoke, *J. Inorg. Nucl. Chem.*, *31*, 2117 (1969).
[4] W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, *5*, 47 (1969), particularly p. 108; C. Oldham, *Prog. Inorg. Chem.*, *10*, 223 (1968), particularly p. 248.
[5] E. Kokot and R. L. Martin, *Inorg. Chem.*, *3*, 1306 (1964).
[6] G. Narain, *Can. J. Chem.*, *44*, 895 (1966) and references therein.
[7] G. J. Tennenhouse and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, *28*, 682 (1966).
[8] G. Brauer, Handbuch der Präparativen Anorganischen Chemie, Ferdinand Enke Verlag, Stuttgart, 1954, p. 762.
[9] Metal analyses (by EDTA titration using PAN indicator) gave excellent and reproducible results, but carbon and hydrogen analyses on several differentsamples by three commercial microanalysts gave varying and low results, suggesting instability of the complex.

Table I. Electronic Spectra of the Complexes, λ_{max}, mμ (ε)

Complex	Band I	Band II	Method
$Cu(C_2H_3O_2)_2 . DMF$	692 (81)	371 (32)	DMF solution
$Cu(C_2H_3O_2)_2 . TMEN$	667 (132)	Absent	DMF solution
$Cu(C_2H_3O_2)_2 . TMEN$	750	Absent	Reflectance
$Cu(C_2H_3O_2)_2 . QUIN$	710	365 sh	Reflectance
$Cu(C_2H_3O_2)_2 . ½TEDA$	725	355 sh	Reflectance

Table II. Magnetic Data

$[Cu(C_2H_3O_2)_2(TMEN)]$ M.W. 297.84; Diamagnetic Correction 160×10^{-6}; TIP 79×10^{-6}; μ_{eff} 1.82 B.M.

Temp. °K	76.7	157.5	188.2	268.1	296.4	344.0
$10^6\chi_M$(uncorr.)	5415	2597	2103	1507	1352	1111

$[Cu(C_2H_3O_2)_2(DMF)]_2$ M.W. 509.46; Diamagnetic Correction 224×10^{-6}; TIP 120×10^{-6} (assumed)

Temp. °K	84.4	161.2	192.1	269.3	295.3	342.4
$10^6\chi_M$(uncorr.)	−200	1043	1004	1365	1405	1540
$K_{sing \rightleftharpoons trip}$	—	.1950	.2313	.5365	.6485	.9874
μ_{eff} B.M.	0	1.22	1.31	1.78	1.89	2.12

$[Cu(C_2H_3O_2)_2(QUIN)]_2$ M.W. 585.62; Diamagnetic Correction 304×10^{-6}; TIP 120×10^{-6} (assumed)

Temp. °K	76.8	159.5	190.6	269.8	294.1	340.9
$10^6\chi_M$(uncorr.)	11	732	802	1651	1625	1815
$K_{sing \rightleftharpoons trip}$	—	.1480	.1988	.7762	.8855	1.510
μ_{eff} B.M.	0	1.08	1.23	1.99	2.06	2.34

$[Cu(C_2H_3O_2)_2(TEDA)_{1/2}]_2$ M.W. 475.42; Diamagnetic Correction 216×10^{-6}; TIP 120×10^{-6} (assumed)

Temp. °K	85.4	164.1	196.6	275.0	297.4	348.4
$10^6\chi_M$(uncorr.)	154	1125	1151	1377	1480	1565
$K_{sing \rightleftharpoons trip}$	.019	.2148	.2762	.5565	.7058	1.044
μ_{eff} B.M.	.41	1.26	1.40	1.80	1.94	2.15

same way, using a mole ratio of amine: copper slightly greater than 1.0. It was dried *in vacuo* over phosphorus(V) oxide. *Anal.* Calcd. for $CuC_{11}H_{19}NO_4$: Cu, 21.70; C, 45.12; H, 6.54. Found: Cu, 21.62; C, 45.11; H, 6.67.

Physical Measurements. Solution spectra were obtained using 1 cm quartz cells with a Coleman Hitachi Model 124 double beam spectrophotometer connected to a Beckman Microspec recorder. Reflectance spectra were obtained with the standard attachment to the Beckman DK 2 spectrophotometer, using barium sulfate as the standard. In both cases, the wavelength was calibrated with a holmium oxide filter. Magnetic susceptibilities were measured by the Gouy method at liquid nitrogen, carbon disulfide slush, Dry Ice acetone, ice, room, and hot water bath temperatures. A plastic glove bag was cut and taped down over a Mettler H 16 semi-micro balance. A glass sheath containing the suspended Gouy tube extended below the balance into a Dewar flask, which fit into the 1.5" air gap of an Alpha AL 7500 water cooled electromagnet with 4" pole faces. The field strength was about 5 Kgauss. Except during actual measurement, a dry nitrogen stream entered the sheath and exited through the glove bag. Temperatures were measured with a copper-constantan thermocouple placed inside the sheath adjacent to the Gouy tube. The tube constant was redetermined at each temperature of interest, using mercury(II) tetrathiocyanatocobaltate(II) as calibrant. Values for the susceptibility of the calibrant as a function of temperature were calculated by the equations[10]

$$\chi_g = (\chi_M^{corr} - \text{Diamag. Corr.})/\text{M.W.} \qquad \text{cgsemu}$$

$$\chi_M^{corr} = 2.363/(T+\theta) + \text{TIP} \qquad \text{cgsemu}$$

where the diamagnetic correction is 137×10^{-6}, the molecular weight is 491.84, the Weiss temperature θ is 10°, and the temperature independent paramagnetism is 428×10^{-6}.

Results and Discussion

The lower steric requirement of quinuclidine compared to triethylamine is reflected in the formation of the complex $Cu(C_2H_3O_2)_2$: QUIN in dimethylformamide solution; triethylamine is unable to displace the solvent from the coordination sphere of copper(II). The bicyclic diamine TEDA and the open-chain diamine TMEN differ in the formulas of their copper(II) acetate complexes, giving $Cu(C_2H_3O_2)_2 \cdot 1/2$TEDA and $Cu(C_2H_3O_2)_2 \cdot$ TMEN respectively.

The electronic spectra of the complexes are given in Table I. They all show the broad structureless absorption at about 700 mμ typical of d–d transitions in such copper(II) complexes, as well as intense charge-transfer absorption in the ultraviolet. Of spe-

---

(10) F. A. Cotton, *et. al.*, *J. Am. Chem. Soc.*, 83, 4157 (1961); B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

cial interest is Band II, at about 28 kK. While there has been controversy about the assignment of this transition, nevertheless it appears to be diagnostic for the dimer structure of the $[Cu(C_2H_3O_2)_2 \cdot H_2O]_2$ type.[11] Band II is absent in the spectrum of the TMEN complex, both in reflectance and i ndimethylformamide solution. It is resolved for the DMF complex (solution), and is clearly apparent as a broad shoulder on the rising absorption into the ultraviolet of the bicyclic amine complexes (reflectance).

The magnetic data are given in Table II. The TMEN complex is magnetically normal, with a temperature-independent $\mu_{eff} = 1.82$ B.M. A plot of χ_M (corrected for diamagnetism using Pascal's constants) *vs.* 1/T has an intercept of 79×10^{-6} cgsemu, which is taken as the temperature independent paramagnetism (TIP). Aplot of $1/\chi_M$ (corrected for diamagnetism and TIP) *vs.* T is linear and has an intercept of −4°K, corresponding to the Weiss temperature θ.

The other complexes all show antiferromagnetic behavior typical of dimeric copper(II) acetate systems, with a singlet ground state and a triplet excited state. The data were treated according to the method of Hatfield, *et. al.*,[12] except that the TIP correction throughout was taken as 60×10^{-6} cgsemu per copper atom. It is assumed that the magnetic moment of the singlet state is zero, and of the triplet state is $g[S(S+1)]^{1/2} = 3.01$ B.M., using the value $g = 2.13$ reported for copper(II) acetate monohydrate.[13] The mole fractions of singlet and triplet state complexes are calculated at each temperature from the observed susceptibilities; if a system were all in the triplet state the susceptibility $\chi_M^{corr} - TIP$ would be $(3.01/2.828)^2$ (1/T). The singlet $\rightleftharpoons$ triplet equilibrium constants obtained from the mole fractions are used in a plot of ln K *vs.* 1/T, which is fitted by linear least squares to give $-\Delta H/R$ as the slope and $\Delta S/R$ as the intercept. The value of ΔH is taken to be the energy of separation 2J between the two spin states. The increase in spin degeneracy makes a contribution of 2.2 e.u. to the entropy change. The results are given in Table III.

Table III. Singlet→Triplet Energy Separations[a]

Complex	$\Delta H(=2J)$	ΔS
$[Cu(C_2H_3O_2)_2(TEDA)_{1/2}]_2$	302 ± 13 cm^{-1}	2.2 ± 0.2 e.u.
$[Cu(C_2H_3O_2)_2(DMF)]_2$	344 ± 42	2.6 ± 0.5
$[Cu(C_2H_3O_2)_2(QUIN)]_2$	495 ± 49	4.7 ± 0.6

[a] Uncertainties indicated are based on the standard deviation of slope and intercept in the linear regression analysis.

The singlet-triplet energy differences may be compared to the values reported[5] for copper(II) acetate adducts with water (284 cm^{-1}) and pyridine (325 cm^{-1}). It may be significant that the largest energy separation is found for the complex of the strongest base,[2] QUIN.

The spectral and magnetic data indicate that the TMEN complex does not have, and the DMF, QUIN, and TEDA complexes do have, the dimeric structure of the copper(II) acetate monohydrate type. The structure of $Cu(C_2H_3O_2)_2 \cdot 1/2$TEDA is most likely a long chain of copper acetate dimeric units bridged by bidentate diamine units similar to that postulated for $Cu(RCOO)_2 \cdot 1/2$Dioxane.[14]

Acknowledgments. We wish to thank the Oregon State University Research Council and General Research Fund for equipment founds.

---

(11) L. Dubicki and R. L. Martin, *Inorg. Chem.*, 5, 2203 (1966) and references therein.

(12) W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, 2, 629 (1963).

(13) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(14) R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2960 (1959).