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A Quasi-Tetrahedral Cu_4 Cluster with Syn–Anti Bridging Carboxylate Groups: Crystal and Molecular Structure and Magnetic Properties

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The complex $[Cu_4(L)_3(LH)(NO_3)(H_2O)]\cdot 2H_2O$, L and LH representing the dideprotonated and the monodeprotonated forms, respectively, of 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil, has been prepared, investigated by single-crystal X-ray analysis, and characterized through magnetic susceptibility and spectroscopic measurements. It crystallizes in the monoclinic space group $P2_1/c$ with cell constants a = 12.43 (8) Å, b = 41.95 (4) Å, c = 14.77 (7) Å, β = 105.45 (5°), Z = 4, R = 0.130, and R_w = 0.113. The framework of the structure is a 16-membered $(\text{–O–C–O–Cu})_4$ ring involving bridging carboxylate groups in the syn–anti conformation. The ring is folded in such a way that the copper atoms fall at the corners of a distorted tetrahedron. The magnetic study points to a ferromagnetic ground state. The magnitude of the magnetic interaction is discussed on the basis of structural data.

Introduction

The carboxylate group can provide an efficient exchange pathway in copper compounds when the triatomic bridging network –O–C–O– is of the syn–syn type. This is illustrated by the hydrated copper acetate in which two copper ions are bridged symmetrically by four acetate groups. Thi dinuclear complex displays an antiferromagnetic interaction with a singlet–triplet separation of ca. 300 cm^{-1}.[1-3] However the carboxylate group is known to assume other types of bridging, i.e. monoatomic,[4] triatomic anti–anti,[5] and triatomic anti–syn. Complexes involving this last bridging mode are characterized by feeble magnetic interactions that can be either ferromagnetic with J values ranging from ca. 0.5[5-8] to 6.9 cm^{-1} or, in two instances, antiferromagnetic with J values of 1.0[9] and 3.0 cm^{-1}.[10] Analysis of the orbital mechanisms that determine the magnetic interactions in these complexes have been performed at various levels of sophistication.[11]

As expected on the basis of their respective geometries, the syn–syn configuration favors the formation of dinuclear complexes while the anti–anti and syn–anti configurations generally correspond to chain or layer compounds.[12] Surprisingly, we succeeded in obtaining a tetranuclear complex with four bridging CO_2 groups in the syn–anti configuration. The resulting framework is a $(\text{–O–C–O–Cu})_4$ ring folded in such a manner that the four copper ions fall at the corners of a pseudotetrahedron.

The present paper is devoted to the structural and magnetochemical studies of this complex, which derives from the 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil ligand (abbreviated as LH_2 in the following).

Experimental Section

Synthesis and Characterization. The ligand LH_2 was prepared by coupling diazotized anthranilic acid with 6-amino-1,3-dimethyluracil (according to the method described by Lythgoe et al.).[13] The compound was recrystallized from hot pyridine with a yield of 85%; mp 280.8 °C. Anal. Calcd for $C_{13}H_{13}N_5O_4$: C, 51.49; H, 4.32; N, 23.09. Found: C, 51.49; H, 4.33; N, 23.28.

The complex $[Cu_4(L)_3(LH)(NO_3)(H_2O)]\cdot 2H_2O$ was prepared by adding solid copper nitrate trihydrate (0.8 g, 3.3 mmol) to a stirred suspension of freshly prepared LH_2 (1.0 g, 3.3 mmol) in 100 mL of an ethanol/water mixture (20/1) at 5 °C. After 30 min a black homogeneous solution was obtained and allowed to stand at room temperature for 2 days, whereupon black crystals separated. They were filtered off, washed with ethanol, and air-dried; yield 83%.

Anal. Calcd for $Cu_4C_{52}H_{51}N_{21}O_{22}$: C, 40.38; H, 3.20; N, 19.01; Cu, 15.99. Found: C, 39.62; H, 3.26; N, 18.66; Cu, 16.13.

The diffuse-reflectance spectrum displays in the (30–10) × 10^3 cm^{-1} region three absorptions (28.6 × 10^3, 22.2 × 10^3, and 20.8 × 10^3 cm^{-1}) that are attributable to ligand and charge-transfer transitions. A broad band centered at 16.7 × 10^3 cm^{-1} and an ill-resolved shoulder at 14.8 × 10^3 cm^{-1} are most likely attributable to d–d transitions. These spectral features are consistent with the occurrence of CuO_3N_2 chromophores adopting geometries intermediate between square pyramidal and trigonal bipyramidal.[4,14,15]

Table I. Crystallographic Data for $[Cu_4(DZB)_3(DZBH)(NO_3)(H_2O)]\cdot 2H_2O$

chem formula: $C_{52}H_{51}N_{21}O_{22}Cu_4$
space group: monoclinic, $P2_1/c$
fw = 1577.5
a = 12.43 (8) Å
b = 41.95 (4) Å
c = 14.77 (7) Å
β = 105.45 (5)°
V = 7423 (9) $Å^3$
Z = 4
T = 20 °C
$\lambda(\text{Mo K}\alpha)$ = 0.71069 Å
2θ limits: 3° < 2θ < 40°
scan speed: 4–20° min^{-1}
no. of reflns measd = 7520
no. of reflns with $F > 6\sigma(F)$ = 1767
R = 0.13
R_w = 0.11

Physical Measurements. Electronic spectra were obtained with a Varian Cary 2300 spectrometer. EPR spectra were recorded at X-band frequencies with a Bruker 200 TT spectrometer operating at 9.4–9.5 GHz.

Magnetic susceptibility data were collected on powdered samples of the title compound with use of a Faraday type magnetometer fitted with a helium continuous-flow cryostat. Independence of the magnetic susceptibility vs magnetic field was checked at each temperature. Mercury tetrakis(thiocyanato)cobaltate (susceptibility at 20 °C = 16.44 × 10^{-6} cgsu) was used as susceptibility standard. All data were corrected for

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(1) Lewis, J.; Mabbs, F. E.; Royston, L. K.; Smail, W. R. *J. Chem. Soc. A* **1969**, 291.
(2) Martin, R. L.; Watermann, R. *J. Chem. Soc.* **1957**, 2545.
(3) Güdel, H. U.; Stebler, A.; Furrer, A. *Inorg. Chem.* **1979**, *18*, 1021-1023.
(4) Costes, J. P.; Dahan, F.; Laurent, J. P. *Inorg. Chem.* **1985**, *24*, 1018-1022 and references therein.
(5) Inoue, M.; Kubo, M. *Inorg. Chem.* **1970**, *9*, 2310-2314.
(6) Kolks, G.; Lippard, S. J.; Waszczack, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 4832-4833.
(7) Corvan, P. J.; Estes, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1980**, *19*, 1297-1300.
(8) Towle, D. K.; Hoffmann, S. K.; Hatfield, W. E.; Singh, P.; Chaudhuri, P. *Inorg. Chem.* **1988**, *27*, 394-399.
(9) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 2328-2336.
(10) Carlin, R. L.; Kopinga, K.; Kahn, O.; Verdaguer, M. *Inorg. Chem.* **1986**, *25*, 1786-1789.
(11) Albonico, C.; Bencini, A. *Inorg. Chem.* **1988**, *27*, 1934-1940 and references therein.
(12) In the case of $[Cu_2(OAc)_2A]_n$ where A is a macrocyclic ligand, syn–anti carboxylate bridges result in a pseudodinuclear structure (cf. ref 9).
(13) Lythgoe, B.; Tood, A. R.; Topham, A. *J. Chem. Soc.* **1944**, 315-317.
(14) Brown, S. J.; Tao, X.; Stephan, D. W.; Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 3377-3384.
(15) Curtis, N. F.; Einstein, F. W. B.; Morgan, K. R.; Willis, A. C. *Inorg. Chem.* **1985**, *24*, 2026-2032.

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Table II. Fractional Atomic Coordinates for $[Cu_4(DZB)_3(DZBH)(NO_3)(H_2O)]\cdot 2H_2O$

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cu(101)	0.2352 (6)	0.3611 (2)	−0.1436 (5)	Cu(201)	0.3916 (7)	0.3352 (2)	0.1694 (5)
O(102)	0.328 (3)	0.353 (2)	−0.030 (2)	O(202)	0.403 (7)	0.380 (1)	0.184 (3)
C(103)	0.432 (2)	0.351 (1)	−0.002 (2)	C(203)	0.390 (5)	0.398 (1)	0.247 (3)
O(104)	0.490 (3)	0.342 (2)	0.076 (2)	O(204)	0.405 (7)	0.427 (1)	0.252 (3)
C(105)	0.509 (4)	0.355 (1)	−0.068 (4)	C(205)	0.375 (4)	0.384 (2)	0.338 (2)
C(106)	0.612 (4)	0.339 (1)	−0.049 (3)	C(206)	0.396 (3)	0.404 (1)	0.418 (3)
C(107)	0.678 (2)	0.342 (1)	−0.112 (2)	C(207)	0.386 (2)	0.391 (1)	0.503 (2)
C(108)	0.641 (3)	0.360 (1)	−0.194 (2)	C(208)	0.355 (2)	0.359 (1)	0.508 (2)
C(109)	0.538 (3)	0.376 (1)	−0.213 (3)	C(209)	0.334 (3)	0.340 (1)	0.428 (3)
C(110)	0.472 (3)	0.373 (1)	−0.150 (4)	C(210)	0.344 (4)	0.353 (2)	0.343 (2)
N(111)	0.354 (3)	0.385 (1)	−0.171 (2)	N(211)	0.307 (3)	0.330 (1)	0.266 (3)
N(112)	0.348 (3)	0.412 (1)	−0.221 (2)	N(212)	0.239 (3)	0.307 (1)	0.267 (3)
C(113)	0.254 (3)	0.427 (1)	−0.251 (1)	C(213)	0.203 (2)	0.2861 (5)	0.199 (2)
C(114)	0.145 (4)	0.4155 (5)	−0.257 (2)	C(214)	0.245 (2)	0.280 (1)	0.120 (2)
N(115)	0.055 (3)	0.433 (1)	−0.301 (2)	N(215)	0.207 (1)	0.254 (1)	0.066 (1)
C(116)	0.066 (2)	0.461 (1)	−0.347 (1)	C(216)	0.125 (1)	0.234 (1)	0.083 (1)
N(117)	0.169 (2)	0.4722 (4)	−0.345 (1)	N(217)	0.085 (1)	0.2401 (4)	0.158 (1)
C(118)	0.266 (2)	0.456 (1)	−0.301 (1)	C(218)	0.119 (2)	0.2655 (5)	0.218 (1)
O(119)	0.358 (2)	0.467 (1)	−0.302 (2)	O(219)	0.079 (2)	0.270 (1)	0.284 (1)
C(120)	0.181 (4)	0.5033 (5)	−0.389 (2)	C(220)	0.003 (2)	0.218 (1)	0.180 (2)
O(121)	−0.017 (2)	0.476 (1)	−0.387 (1)	O(221)	0.093 (2)	0.2114 (5)	0.032 (1)
C(122)	−0.059 (4)	0.422 (1)	−0.307 (2)	C(222)	0.247 (2)	0.247 (1)	−0.018 (2)
N(123)	0.125 (2)	0.387 (1)	−0.223 (2)	N(223)	0.325 (3)	0.295 (1)	0.115 (3)
Cu(301)	0.3922 (7)	0.4314 (2)	0.1028 (5)	Cu(401)	0.0477 (6)	0.3947 (2)	0.0723 (5)
O(302)	0.2316	0.4280	0.0708	O(402)	0.0842	0.3720	−0.0282
C(303)	0.1446	0.4408	0.0224	C(403)	0.0788	0.3438	−0.0567
O(304)	0.0457	0.4330	0.0153	O(404)	0.1276	0.3316	−0.1121
C(305)	0.181 (8)	0.471 (1)	−0.035 (3)	C(405)	0.003 (4)	0.321 (1)	−0.020 (4)
C(306)	0.093 (5)	0.491 (1)	−0.074 (2)	C(406)	−0.039 (3)	0.294 (1)	−0.073 (3)
C(307)	0.111 (3)	0.517 (1)	−0.129 (2)	C(407)	−0.115 (2)	0.274 (1)	−0.045 (2)
C(308)	0.216 (3)	0.522 (1)	−0.144 (2)	C(408)	−0.149 (2)	0.281 (1)	0.036 (2)
C(309)	0.304 (3)	0.501 (1)	−0.105 (2)	C(409)	−0.107 (4)	0.308 (1)	0.089 (3)
C(310)	0.286 (6)	0.475 (1)	−0.050 (3)	C(410)	−0.031 (5)	0.328 (1)	0.061 (4)
N(311)	0.382 (3)	0.457 (1)	−0.012 (3)	N(411)	0.023 (3)	0.356 (1)	0.119 (2)
N(312)	0.462 (3)	0.456 (1)	−0.057 (2)	N(412)	0.019 (3)	0.346 (1)	0.210 (3)
C(313)	0.552 (1)	0.438 (1)	−0.037 (2)	C(413)	0.045 (1)	0.3706 (5)	0.276 (1)
C(314)	0.596 (2)	0.419 (1)	0.045 (1)	C(414)	0.050 (1)	0.3580 (4)	0.366 (1)
N(315)	0.698 (2)	0.4057 (5)	0.059 (1)	N(415)	0.082 (1)	0.3770 (4)	0.443 (1)
C(316)	0.764 (1)	0.4111 (4)	−0.002 (1)	C(416)	0.106 (1)	0.4092 (4)	0.435 (1)
N(317)	0.723 (1)	0.4289 (4)	−0.080 (1)	N(417)	0.102 (1)	0.4214 (4)	0.349 (1)
C(318)	0.620 (1)	0.4433 (5)	−0.101 (1)	C(418)	0.071 (1)	0.4038 (5)	0.267 (1)
O(319)	0.587 (2)	0.460 (1)	−0.172 (1)	O(419)	0.067 (2)	0.416 (1)	0.191 (1)
C(320)	0.791 (2)	0.433 (1)	−0.149 (1)	C(420)	0.135 (2)	0.4550 (4)	0.342 (2)
O(321)	0.856 (2)	0.399 (1)	0.014 (1)	O(421)	0.133 (2)	0.4257 (5)	0.505 (1)
C(322)	0.747 (3)	0.387 (1)	0.144 (1)	C(422)	0.086 (2)	0.365 (1)	0.537 (1)
N(323)	0.551 (3)	0.419 (1)	0.115 (2)	N(423)	0.026 (2)	0.3277 (4)	0.378 (2)
O(501)	0.239 (3)	0.328 (1)	−0.274 (3)	O(505)	0.552 (5)	0.325 (1)	0.281 (4)
N(502)	0.301 (2)	0.305 (1)	−0.247 (2)	O(506)[a]	0.184 (5)	0.908 (2)	0.121 (4)
O(503)	0.326 (4)	0.297 (1)	−0.164 (2)	O(507)[a]	0.296 (5)	0.907 (2)	0.147 (4)
O(504)	0.338 (4)	0.290 (1)	−0.305 (3)	O(508)	0.421 (5)	0.973 (1)	0.134 (4)

[a] Population parameters 0.5.

diamagnetism of the ligands and anion estimated from Pascal constants[16] and for TIP.

X-ray Data Collection and Structure Determination and Refinement. Numerous attempts to crystallize a specimen suitable for X-ray data collection yielded only irregularly shaped crystals. Several crystals were examined on the Nicolet P3F diffractometer. The peak profiles were found to be highly broadened and the diffraction power was modest even at low reflection angles.

The cell parameters were obtained by least-squares refinement of 20 accurately centered reflections. The crystals of the compound proved to be highly unstable even in the capillary tube. The crystal chosen for the data collection was covered with two-component epoxy glue and placed into the capillary tube. Because of the tendency to decay and due to the poor scattering power, limited data were collected at high scan speeds (cf. Table I). Systematic absences uniquely specified the space group $P2_1/c$. The data were corrected for Lorentz and polarization effects and for decay (20%). ψ scans for several intense reflections verified the absence of noteworthy variable absorption. In keeping with the very poor crystal quality and very poor statistics of the small reflections, the main interest was focused on the coordination mode of the ligands and the most general features of the structure. Therefore two criteria were used to limit the data: 2300 reflections having $F > 4\sigma(F)$ and 1767 reflections with $F > 6\sigma(F)$ were considered as observed in refinements of individual non-hydrogen atoms and final rigid-group refinements, respectively.

Positions of the four independent copper atoms were obtained from the Patterson map calculated by SHELXS-86.[17] A series of subsequent Fourier maps and refinements by the XTAL program system[18] revealed almost 80 more atoms of the tetrameric unit: the oxygen atoms of the nitrate ion and two single maxima, which were identified as oxygen atoms of crystal water molecules (coordinated O(505) and noncoordinated O(508) water oxygens). The rest of the non-hydrogen atoms of the tetrameric unit and the nitrogen atom of the NO_3^- ion (labeled O(501)–O(504) were placed at the calculated or estimated positions. Moreover, two maxima of 1.5 e Å^{-3} at a distance of about 1.5 Å were considered as positions of disordered oxygen atoms of crystal water molecules (labeled O(506) and O(507)); the occupancy factors of the atom were fixed as 0.5 in the refinements. Refinement of all non-hydrogen atoms (the copper atoms anisotropically and the other non-hydrogen atoms isotropically) reduced the R value to 0.16 for 2300 reflections.

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(16) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5.

(17) Sheldrick, G. M. SHELX-86. Program for Crystal Structure Solution. University of Gottingen, FRG, 1986.

(18) Hall, S. R.; Stewart, J. M., Eds. XTAL2.2 User's Manual. Universities of Western Australia and Maryland, March 1987.

Table III. Interatomic Distances (Å) and Bond Angles (deg)

Cu(101)–O(102)	1.80 (3)	Cu(201)–O(104)	2.09 (4)
Cu(101)–N(111)	1.91 (4)	Cu(201)–O(202)	1.88 (3)
Cu(101)–N(123)	1.89 (3)	Cu(201)–N(211)	2.00 (5)
Cu(101)–O(404)	1.97	Cu(201)–N(223)	1.97 (4)
Cu(101)–O(501)	2.37 (4)	Cu(201)–O(505)	2.26 (5)
C(103)–C(105)	1.55 (7)	C(203)–C(205)	1.53 (6)
C(110)–N(111)	1.50 (5)	C(210)–N(211)	1.47 (7)
N(111)–N(112)	1.34 (5)	N(211)–N(212)	1.27 (6)
N(112)–C(113)	1.30 (5)	N(212)–C(213)	1.31 (4)
C(114)–N(123)	1.34 (4)	C(214)–N(223)	1.19 (5)
Cu(301)–O(202)	2.47 (3)	Cu(401)–O(304)	1.81
Cu(301)–O(204)	2.17 (4)	Cu(401)–O(321)^a	2.31 (2)
Cu(301)–O(302)	1.93	Cu(401)–O(402)	1.91
Cu(301)–N(311)	1.98 (4)	Cu(401)–N(411)	1.81 (4)
Cu(301)–N(323)	2.00 (4)	Cu(401)–O(419)	1.93 (2)
C(303)–C(305)	1.64	C(403)–C(405)	1.54
C(310)–N(311)	1.41 (8)	C(410)–N(411)	1.50 (5)
N(311)–N(312)	1.34 (6)	N(411)–N(412)	1.42 (6)
N(312)–C(313)	1.31 (4)	N(412)–C(413)	1.40 (4)
C(314)–N(323)	1.30 (5)	C(414)–N(423)	1.33 (3)
O(102)–Cu(101)–N(111)	87 (2)	O(104)–Cu(201)–O(202)	85 (3)
O(102)–Cu(101)–N(123)	150 (3)	O(104)–Cu(201)–N(211)	176 (1)
O(102)–Cu(101)–O(404)	88	O(104)–Cu(201)–N(223)	96 (3)
O(102)–Cu(101)–O(501)	120 (3)	O(104)–Cu(201)–O(505)	87 (2)
N(111)–Cu(101)–N(123)	92 (1)	O(202)–Cu(201)–N(211)	94 (3)
N(111)–Cu(101)–O(404)	172	O(202)–Cu(201)–N(223)	156 (2)
N(111)–Cu(101)–O(501)	87 (2)	O(202)–Cu(201)–O(505)	94 (2)
N(123)–Cu(101)–O(404)	95	N(211)–Cu(201)–N(223)	87 (2)
N(123)–Cu(101)–O(501)	90 (1)	N(211)–Cu(201)–O(505)	89 (2)
O(404)–Cu(101)–O(501)	89	N(223)–Cu(201)–O(505)	109 (2)
Cu(101)–O(102)–C(103)	132 (3)	Cu(201)–O(202)–C(203)	133 (4)
C(103)–O(104)–Cu(201)	111 (3)	C(203)–O(204)–Cu(301)	92 (3)
Cu(101)–N(111)–C(110)	124 (3)	Cu(201)–N(211)–C(210)	111 (3)
Cu(101)–N(111)–N(112)	129 (3)	Cu(201)–N(211)–N(212)	125 (3)
Cu(101)–N(123)–C(114)	124 (3)	Cu(201)–N(223)–C(214)	134 (3)
O(202)–Cu(301)–O(204)	57 (1)	O(304)–Cu(401)–O(321)^a	83
O(202)–Cu(301)–O(302)	88	O(304)–Cu(401)–O(402)	93
O(202)–Cu(301)–N(311)	151 (2)	O(304)–Cu(401)–N(411)	170
O(202)–Cu(301)–N(323)	79 (2)	O(304)–Cu(401)–O(419)	90
O(204)–Cu(301)–O(302)	92	O(321)^a–Cu(401)–O(402)	101
O(204)–Cu(301)–N(311)	152 (2)	O(321)^a–Cu(401)–N(411)	87 (1)
O(204)–Cu(301)–N(323)	95 (2)	O(321)^a–Cu(401)–O(419)	100 (1)
O(302)–Cu(301)–N(311)	90	O(402)–Cu(401)–N(411)	87
O(302)–Cu(301)–N(323)	159	O(402)–Cu(401)–O(419)	160
N(311)–Cu(301)–N(323)	93 (2)	N(411)–Cu(401)–O(419)	93 (1)
Cu(301)–O(302)–C(303)	142	Cu(401)–O(402)–C(403)	137
C(303)–C(304)–Cu(401)	108	Cu(101)–O(404)–C(403)	112
Cu(301)–N(311)–C(310)	120 (4)	Cu(401)–N(411)–C(410)	125 (3)
Cu(301)–N(311)–N(312)	121 (3)	Cu(401)–N(411)–N(412)	133 (3)
C(316)^a–O(321)^a–Cu(401)	158 (2)	Cu(401)–O(419)–C(418)	127 (2)
Cu(301)–N(323)–C(314)	124 (2)		

[a] Equivalent position $x - 1, y, z$.

This result is based on the assumption that each of the four LH_2 ligands coordinated in their dianionic form L^{2-} through deprotonated 6-amino nitrogen atoms. However, abnormal bond lengths and angles and temperature factors were obtained for about 10 atoms. Careful refinements using only 1767 reflections reduced the R value to 0.115, but the resolution was not improved. Since further improvement was not possible, the rigid-body method was employed by using the program system XTAL.

The following rigid atom groups were included in the refinements: phenyl group C_6H_4, with C–C = 1.40 Å and C–H = 1.00 Å; carboxylate group with C–O = 1.25 Å and O–C–O = 128°; nitrate group with N–O = 1.24 Å. Moreover, the substituted uracil group of a related gold complex $[AuCl_2(LH_2)]\cdot{}^3/_2H_2O$[19] was supposed to be an "ideal" group in the calculations.

Positional and thermal parameters of the copper atoms, the nitrogen atoms of the azo groups, the 6-amino nitrogen of the uracil group, and the oxygen atoms of the crystal water molecules were refined as individual atoms. Only copper atoms were refined anisotropically. The positions and orientations of the rigid groups, as well as individual temperature factors of the atoms of the uracil groups, were refined, except for the carboxylate groups labeled O(302)–O(304) and O(402)–O(404), which were not refined in the final refinement. Rigid-group refinement at this stage results in an R value of 0.135.

It appears that the structure comprises four independent copper(II) atoms and one nitrate ion. Therefore three of the tetradentately acting ligands most probably coordinate as the divalent anionic ligands L^{2-} and one ligand coordinates as the monovalent anionic ligand LH^-. The substituted uracil moiety of L^{2-} coordinates through a deprotonated amino group, but LH^- may coordinate through a deprotonated NH_2 group [N(123)H, for instance] or through a carbonyl oxygen [O(119) for instance]. Critical examination of contact distances together with atomic arrangement of relevant atoms indicates that the ligand labeled O(402)–N(423) coordinates probably through a carbonyl oxygen atom and thus exists as the monovalent anionic ligand LH^- (cf. Table III). Refinement of this arrangement gave the final R value of 0.130 (R_w = 0.113). Except for the phenyl hydrogen atoms, the hydrogen atoms were not included in the calculations. The maximum and minimum peaks in the difference Fourier map were 0.97 and −0.73 e Å^{-3}, respectively. The quantity $w(|F_o| - |F_c|)^2$ was minimized, where $w^{-1} = \sigma^2(F)$.

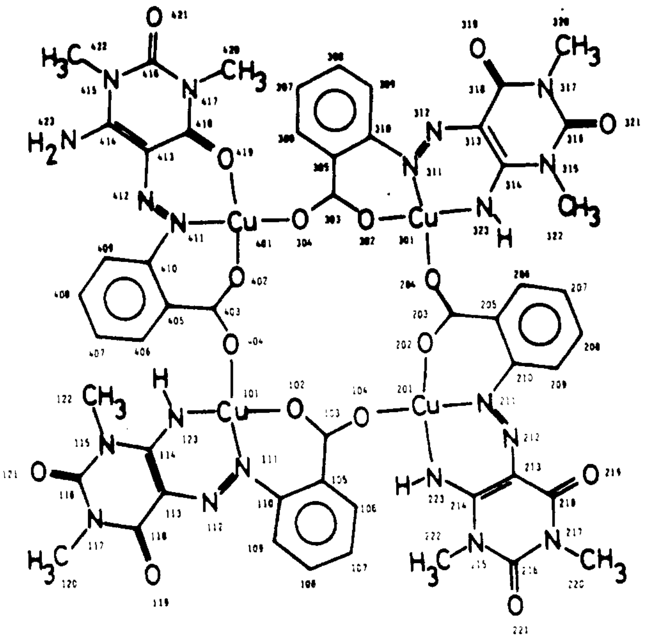

Figure 1. Labeling scheme of the structure.

Obviously, the main reason for the high R value is the poor crystal quality. Probably, the crystals are also only partly crystalline. Moreover, the chosen rigid groups are only approximate. The C—O distances of 1.25 Å are approximate medium values of the C—O and C=O bond lengths of the carboxylate group, and the available bond parameters of the substituted uracil moiety are not very accurate.

The final positional parameters are listed in Table II, while Table III contains a selection of bond distances and angles (the other values appear in supplementary material, Table S6).

Results and Discussion

Description of the Structure. The most interesting feature of the structure (schematized in Figure 1) results from the presence of discrete Cu_4 clusters. Each ligand acts as a bridge between two copper ions via both oxygen atoms of its carboxylato group. This results in the formation of 16-membered ring $(\text{–Cu–O–C–O})_4$ represented in Figure 2. As suggested by microanalytical data and charge balance consideration, the four ligands are not equivalent. Three of them are twice deprotonated, at the carboxylato and amino groups, whereas the fourth one is monodeprotonated at the carboxylic group. The first three ligands link the metal through two nitrogen atoms from the diazo and deprotonated amino groups and one oxygen atom of the carboxylato group. In the last case, the nonionized amino group remains uncoordinated and coordination is achieved via a carbonyl oxygen atom. In addition, the ligand labeled O(302)–N(323), which contributes to the N_2O_2 environment of Cu(301) according to the aforementioned coordination scheme, binds a copper atom of a neighboring cluster through the carbonyl oxygen atom O(321).

The four copper atoms adopt a (4 + 1) coordination mode. Four donors are afforded by the ligands LH_2 whereas, in each case, the fifth coordination site is occupied by an oxygen atom. This oxygen atom belongs to either the nitrato ion in the case of Cu(101), a water molecule for Cu(201), a carboxylato group for Cu(301), or a uracil nucleus from another tetrameric unit for

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(19) Kivekäs, R.; Colacio, E.; Ruiz, J.; Lopez-Gonzalez, J. D.; Leon, P. *Inorg. Chim. Acta* **1989**, *159*, 103-110.

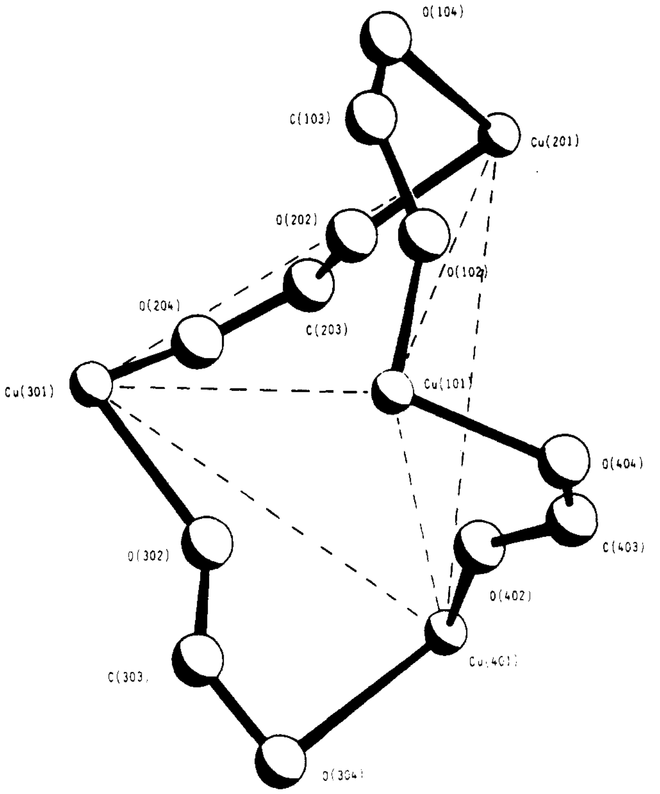

Figure 2. Perspective view of the 16-membered ring.

Cu(401). It may be emphasized that an unusual bridging scheme is achieved between Cu(201) and Cu(301) since the same carboxylato group acts simultaneously as a monoatomic bridge through O(202) and a triatomic bridge [O(202), C(203), O(204)] between the pair of copper ions.

The (4 + 1) coordination of each copper atom is compatible with two idealized geometries, i.e. square pyramidal or trigonal bipyramidal. From the values of the angles around the metal centers (Table III), one can see that none of these limiting geometries is achieved. To obtain a quantitative description, we will consider the procedure proposed by Muetterties,[20] which leads to a measure of polytopal shape referenced to idealized geometries, namely C_{4v} and D_{3h} in the present case. From the data of Table S1 (supplementary material) it appears that, for the polyhedra related to Cu(101), Cu(201), and Cu(401) the actual geometry is practically just intermediate between D_{3h} and C_{4v}. As for Cu(301), its coordination polyhedron does not lie on the $D_{3h} \leftrightarrow C_{4v}$ deformation path.

In the square-pyramidal description of the environment around Cu(101), Cu(201), and Cu(401), the basal planes are defined by [N(111), O(102), O(404), N(123)], [N(211), O(202), O(104), N(223)], and [N(411), O(402), O(304), O(419)], respectively, whereas the related apical positions are occupied by O(501), O(505), and O(321), which are coordinated at distances larger than the other donors. A trigonal-pyramidal description places [O(102), O(501), N(123)], [O(202), O(505), N(223)], and [O(402), O(321), O(419)], respectively, in the three equatorial planes and [N(111), O(404)], [N(211), O(104)], and [N(411), O(304)], respectively, at the axial positions. The pseudotrigonal axes do not show too much distortion from linearity, the related N–Cu–O angles varying from ca. 170 to ca. 176°.

The environment around Cu(301), which is not intermediate between square pyramidal and trigonal bipyramidal, is difficult to describe in a simple way. Two descriptions deriving from a square pyramid are conceivable. In the first one (i), the basal plane is defined by [N(311), O(204), O(302), N(323)], the apex being occupied by O(202) in accordance with the long Cu(301)–O(202) distance. The angles subtended by the basal donors do not differ too much from 90° (from ca. 90 to ca. 95°), but the axial bond Cu(301)–O(202) tilts toward one of the equatorial bonds, i.e. Cu(301)–O(204), the O(202)–Cu(301)–O(204) angle being 57 (1)°. The second description (ii) places [N(323), O(202), O(302), N(311)] in the basal plane and O(204) at the axial position. The angles in the basal plane depart more significantly from the theoretical 90° value (from ca. 79 to ca. 93°), but their sum is almost equal to 360°. As in the former description, the axial bond Cu(301)–O(204) tilts toward Cu(301)–O(202). A third description (iii) deriving from a trigonal bipyramid defines the equatorial plane by [O(202), O(204), N(311)] and the trigonal axis by [N(323), O(302)]. This axis does not show too much distortion from linearity, since the related angle is 159 (1)°, but the angles in the trigonal plane differ considerably from the theoretical value of 120° with values of 151 (1), 152 (1), and 57 (1)°, respectively.

Table IV. Interatomic Distances (Å) and Bond Angles (deg) for the Copper Atoms

Cu(101)···Cu(201)	4.641 (9)	Cu(201)···Cu(301)	4.15 (1)
Cu(101)···Cu(301)	4.69 (1)	Cu(201)···Cu(401)	4.83 (1)
Cu(101)···Cu(401)	4.64 (1)	Cu(301)···Cu(401)	4.46 (1)
Cu(201)···Cu(101)···Cu(301)	52.9 (2)	Cu(101)···Cu(301)···Cu(201)	63.0 (2)
Cu(201)···Cu(101)···Cu(401)	62.7 (2)	Cu(101)···Cu(301)···Cu(401)	60.9 (2)
Cu(301)···Cu(101)···Cu(401)	57.2 (2)	Cu(201)···Cu(301)···Cu(401)	68.0 (2)
Cu(101)···Cu(201)···Cu(301)	64.1 (2)	Cu(101)···Cu(401)···Cu(201)	58.7 (2)
Cu(101)···Cu(201)···Cu(401)	58.7 (2)	Cu(101)···Cu(401)···Cu(301)	62.0 (2)
Cu(301)···Cu(201)···Cu(401)	59.0 (2)	Cu(201)···Cu(401)···Cu(301)	53.0 (2)

In the three descriptions, the principal departure from an ideal geometry arises from the low value of the O(202)–Cu(301)–O(204) angle.

The four bridging carboxylate groups adopt a syn–anti conformation. In the square pyramidal description of the Cu(101), Cu(201), and Cu(401) environments, each carboxylate bridges from a basal position at one copper to a basal position at the other copper atom. The same situation holds for Cu(301) if description i is retained, but description ii results in a bridge from a basal position at Cu(401), to an axial position at Cu(301), i.e. O(204).

If the geometry around the copper atoms is considered as deriving from a trigonal bipyramid, the oxygen atoms of each carboxylate may be either both axial [O(302)/Cu(301) and O(304)/Cu(401)] or both equatorial [O(202)/Cu(201) and O(204)/Cu(301) or one equatorial [O(102)/Cu(101) and O(104)/Cu(201)] and one axial [O(402)/Cu(401) and O(404)/Cu(101)].

The C–O bond lengths display almost identical values in the four carboxylato groups, as do the related O–C–O angles. More important variations affect the Cu–O separation and the C–O–Cu angle. The Cu–O separations vary from 1.80 (3) to 2.17 (4) Å. The two lowest values of ca. 1.80 Å, which are related to Cu(101)–O(102) and Cu(401)–O(304), have to be compared to the lowest value quoted in the literature, i.e. 1.94 (3) Å.[21] The longest Cu–O distances are observed for Cu(301): 2.17 (4) Å for the syn bond and 1.93 Å for the anti bond. The 2.17 (4) Å value suggests that O(204) could be axial with respect to Cu(301) in accordance with description ii. The syn C–O–Cu angles display lower values than those quoted in the literature for similar complexes.[9] The distances Cu–N(azo), from 1.81 (4) to 1.99 (5) Å, and Cu–N(amino), from 1.89 (3) to 1.99 (4) Å, are within the ranges of reported values.

The framework of the cluster is a 16-membered ring $(-O-C-O-Cu)_4$ that is folded in such a way that the four copper atoms fall at the corners of a tetrahedron. The characteristics of this tetrahedron are reported in Table IV. According to the Muetterties procedure,[20] the actual geometry lies on the $T_d \leftrightarrow D_{4h}$ deformation pathway, the T_d character being of 87% (cf. Table S2, supplementary material). The Cu···Cu distances vary from 4.15 (1) to 4.83 (1) Å. Interestingly, the largest separation is observed for two nonbridged copper atoms, namely Cu(201) and Cu(401), whereas the smallest one corresponds to Cu(201) and

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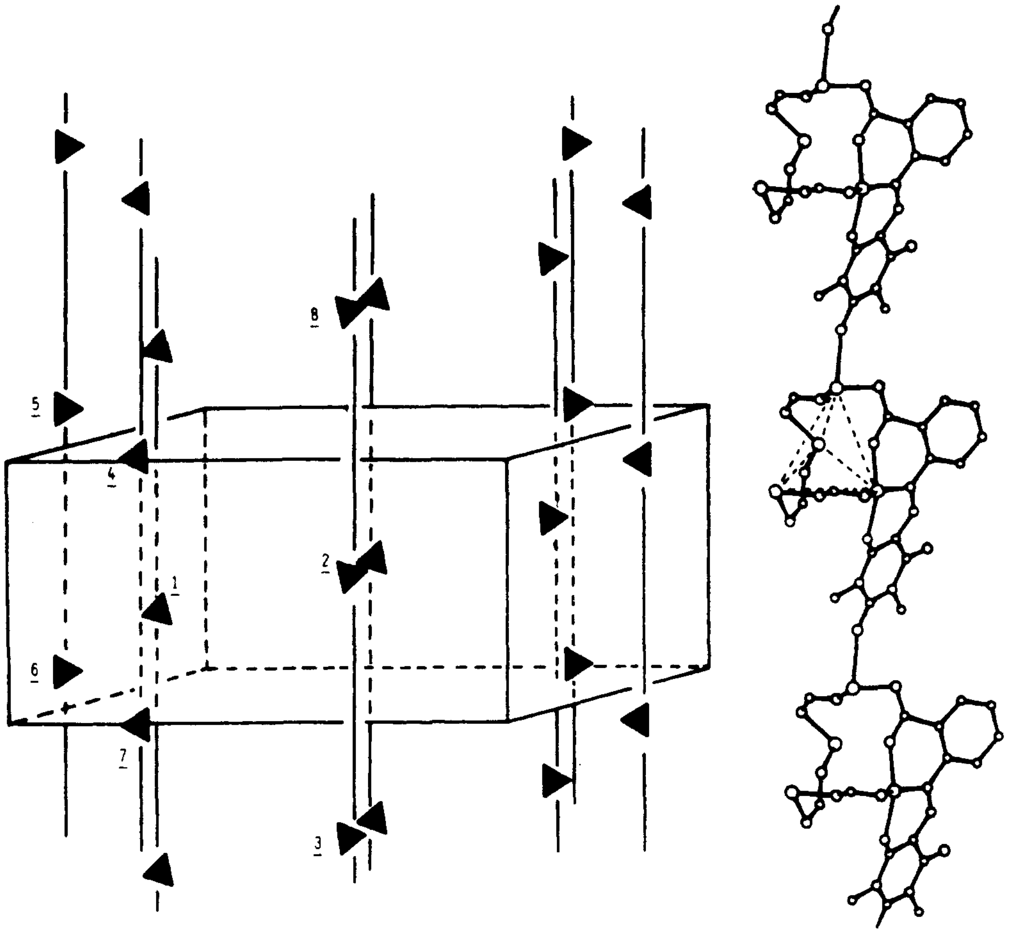
(20) Muetterties, E. L.; Guggenberg, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748–1756.

(21) Whitlow, S. H.; Davey, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1228.



1. $x, y, z,$
2. $-x+1, -y-1; -z$
3. $-x, -y+1, -z$
4. $x, -y+\frac{1}{2}, z+\frac{1}{2}$
5. $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$
6. $-x, y-\frac{1}{2}, -z+\frac{1}{2}$
7. $x-1, -y+\frac{1}{2}, z+\frac{1}{2}$
8. $-x+2, -y+1, -z$

Figure 3. Chains of tetrahedrons parallel to the *a* axis.

Table V. Intermolecular Contacts (Å) and Symmetry Operations[a]

Cu(401)···O(321)^{I}	2.31 (2)	O(504)···N(215)^{V}	2.84 (4)
O(321)···O(304)^{II}	2.75	O(508)···O(119)^{VI}	2.89 (8)
O(421)···N(117)^{III}	2.90 (2)	O(508)···O(204)^{VII}	3.02 (8)
N(423)···O(221)^{IV}	2.75 (3)		

[a] I = $x - 1, y, z$; II = $x + 1, y, z$; III = $x, y, z + 1$; IV = $x, -y + ^1/_2, z + ^1/_2$; V = $x, -y + ^1/_2, z - ^1/_2$; VI = $x, -y + ^3/_2, z + ^1/_2$; VII = $-x + 1, y + ^1/_2, -z + ^1/_2$.

Cu(301), which are linked by two bridges, a triatomic one and a monoatomic one. The Cu···Cu distances issued from Cu(301) are significantly shorter than the other separations; Cu(301)···Cu(101) and Cu(301)···Cu(401) are the shortest distances between two nonbridged copper and two monobridged copper atoms, respectively. This shortening of the Cu(301)···Cu separations and the folding of the ring likely are due to steric requirements of the bulky ligands and constraints imposed by chelation. These deformations prevent overcrowding in the vicinity of the external faces of the cluster, especially around Cu(401), which is directly involved in binding with a neighboring cluster.

Indeed, the tetranuclear units are linked to each other through Cu(401) of one unit and the oxygen atom O(321) belonging to the pyrimidine bound to Cu(301) in the nearest unit. The net result is the formation of chains of tetrahedrons running parallel to the *a* axis, as represented in Figure 3. The shortest separation between two metal atoms belonging to the same chain is 8.42 (1) Å whereas the shortest interchain Cu···Cu distances are 7.34 (1) and 8.77 (1) Å. The former value corresponds to pairs of chains related by a center of symmetry.

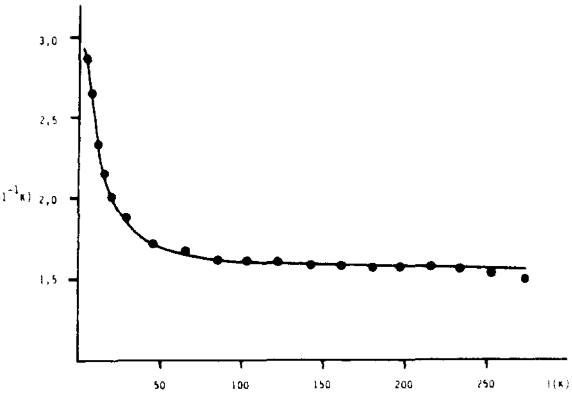


Figure 4. Experimental (●) and calculated (—) temperature dependence of $\chi_M T$ for the title compound.

The most relevant intermolecular contacts are quoted in Table V.

Magnetic Properties. Static Magnetic Susceptibility. The magnetic susceptibility of a powdered sample of the complex was investigated in the temperature range 280–4 K. The temperature dependence of χ^{-1} from 280 to 4 K is well fitted to a Curie–Weiss law with C = 1.514 and Θ = 5.15. This C value is as expected for four copper atoms with g = 2.01. From the positive value of Θ, it can be estimated that the complex displays an overall ferromagnetic behavior. This is also apparent from a consideration of the thermal variation of the product $\chi_M T$, which is represented in Figure 4. From 275 to ca. 100 K, $\chi_M T$ remains practically constant and equal to 1.5 cm^3 mol^{-1} K, which is the value expected for a cluster of four isolated copper ions. On further lowering of the temperature, $\chi_M T$ increases, yielding an extrapolated value of ca. 3 cm^3 mol^{-1} K at 0 K. This value would correspond to a state characterized by a spin of 2 with a g value of 2.01.

Central to the data analysis problem is the choice of a suitable model. For a tetranuclear entity with C_1 symmetry, six exchange integrals J_{ij} and the g values corresponding to the different spin states are needed, leaving us with a problem of overparametrization. A reduction of the number of parameters may be obtained by assuming a symmetry higher than C_1. The structural data could suggest an idealized T_d symmetry. In this instance the temperature dependence of the magnetic susceptibility is represented by the expression[22]

$$\chi_{\text{tetra}} = \frac{Ng^2\beta^2}{kT}\,\frac{10 + 6e^{2u}}{5 + 9e^{2u} + 2e^{3u}}(1 - p) + p\frac{Ng^2\beta^2}{kT} + 4N\alpha$$

which contains a term corresponding to the presence of a small amount (p) of paramagnetic species and where $u = J/kT$. The other symbols have their usual meaning.

A reasonable agreement ($R = 2 \times 10^{-4}$) is obtained with $J = 6.8$ cm^{-1}, $g = 2.01$, and $p = 0.04$. This fit is indicated by the solid line in Figure 4.

A closer examination of the structural data shows that, although the hypothesis of T_d symmetry for the Cu_4 cluster is reasonably good, the assumption that all the J_{ij} are equal is more questionable. Indeed, two pairs of copper atoms, Cu(101)/Cu(301) and Cu(201)/Cu(401), are not joined by any bridging group. In addition simple triatomic bridges are operative for the Cu(101)/Cu(201), Cu(301)/Cu(401), and Cu(401)/Cu(101) pairs whereas Cu(201) and Cu(301) are simultaneously joined by a triatomic and monoatomic bridge. This suggests that the adequacy of the phenomenological model to the actual structure may be improved by increasing the number of distinct values for the coupling constants J_{ij}. In fact, a model of D_{2d} symmetry[22] with two constants, $J = J_{12} = J_{14} = J_{34} = J_{32}$ and $j = J_{13} = J_{24}$, leads only to a slight improvement of the fit ($R = 1 \times 10^{-4}$, with $J = 11$ cm^{-1}, $j = 0$, $g = 2.01$, and $p = 0$).

Finally, the proper conclusion of this study is that the ground state of the Cu_4 cluster is ferromagnetic ($S_T = 2$). Due to the low J value (of the order of ca. 10 cm^{-1}), the excited states ($S_T = 1$ and $S_T = 0$) are not far removed from the ground state with separations of the order of ca. 10 and 30 cm^{-1}, respectively.

EPR Spectroscopy. Due to the proximity of the $S_T = 2$ and $S_T = 1$ states, both multiplets are expected to contribute to the spectrum in a large temperature range. The room-temperature X-band spectrum of a powdered sample shows an intense and quasi-isotropic absorption at $g = 2.12_5$ and a weaker signal at $g = 4.29$. Lowering the temperature from ca. 300 to 5 K does not alter the overall appearance of the spectrum but increases slightly its intensity. Surprisingly, none of the features previously reported for quintet spectra[23,24] are observed. It may be noted that, to our knowledge, EPR signals attributable to transitions within the quintet state have been scarcely ever observed[23] for tetranuclear copper(II) complexes. Generally, these complexes yield spectra[25,26] attributable to the triplet state, as it is seemingly the case for the present complex. Indeed, the experimental spectra are very reminiscent of spectra attributed to dinuclear copper(II) complexes.[27] In this instance the broad signal at $g = 2.12_5$ would be attributable to $\Delta M = 1$ transitions and the weaker one at $g = 4.29$ to $\Delta M = 2$ transitions.

Interestingly, an isotropic signal centered at $g = 2.115$ is also observed for frozen solutions (acetone). When DMSO is used as solvent a very different pattern results: an axial doublet spectrum and two additional absorptions of medium intensity at 3510 and 3040 G, respectively. As for the doublet spectrum, a hyperfine structure with $|A| = 180$ G is clearly seen on the parallel component while five lines of superhyperfine interaction $|A| = 18$ G are discernible on the perpendicular component. From these data, one may conclude that the tetranuclear structure is retained in acetone but not in DMSO solutions. Obviously, DMSO causes the dissociation of the tetranuclear complex into a mononuclear complex responsible of the doublet spectrum and, probably, a dinuclear species. Indeed, the low g value (1.92) associated with one of the two additional signals suggests the occurrence of significant zero-field splitting effects.

Irrespective of the exact assignment of the spectra (powdered sample and frozen solutions in acetone), one may wonder why the related g value of 2.12_5 differs significantly from the value derived from susceptibility data. In fact, this last value of 2.01 is abnormally low. This may result from several factors such as poor evaluation of the diamagnetic and temperature-independent paramagnetic contributions. However we feel that the main factors are related to crudeness of the phenomenological model used to analyze the temperature dependence of the susceptibility. Indeed, this model comprises one "averaged" g value whereas the structure points to the presence of four nonequivalent copper ions. Furthermore there is no obvious reason to attribute the same g values to the different spin states.[28]

As previously noted, the ferromagnetic behavior of the present complex is not unexpected. It has been rationalized on an orbital basis (ref 10 and references therein) in the cases where the geometry at the copper atoms is not far removed from square planar or square pyramidal. The unpaired electron around each metal center can be described by a magnetic orbital of $x^2 - y^2$ type pointing toward the donor atoms located in the basal plane with some possible admixture of a z^2 type orbital. The magnitude of the antiferromagnetic interaction depends on the overlap of the magnetic orbitals centered on nearest-neighbor copper ions. For a syn–anti conformation of the (CU–O–C–O′–Cu′) bridges, the 2p orbitals of O and O′ belonging to the magnetic orbitals centered on Cu and Cu′, respectively, are unfavorably oriented to give a strong overlap. This would cause a reduction of the antiferromagnetic contribution, which would lead ultimately to an overall ferromagnetic behavior. In keeping with this rationale, we must note that the angles between the syn Cu–O bond and the anti Cu–O bond display, in the Cu_4 cluster, a mean value of 97.8°, which is significantly lower than the values previously reported, for instance 113.8° for $[Cu_2(OAc)_2A]_n$.[9] This is likely the main reason that an overall ferromagnetic behavior is observed in the present case although the low site symmetries of the copper ions make the assignment of the magnetic orbitals rather difficult and speculative. If we assume a description deriving from a square pyramid, there is a possible difficulty at the Cu(201)–O(202)–C–O(204)–Cu(301) bridge. Indeed O(204) can be either basal or axial to Cu(301) depending on the chosen description ((i) or (ii); vide supra) whereas O(202) is basal to Cu(201) in both cases. Though the introduction of some d_{z^2} character in the magnetic orbital centered on Cu(301) is expected to delocalize spin density on the axial ligand, namely O(204) in description ii, the resulting bridge from an equatorial to an axial position likely corresponds to a small antiferromagnetic contribution. If the four copper atoms are assumed to adopt trigonal-bipyramidal geometries, some spin density is expected on all the oxygen atoms involved in the bridging framework. However, for each bridge, the two oxygen atoms may occupy, with respect to the bridged copper atoms, either two axial or two equatorial or one axial and one equatorial positions. Owing

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(22) Jotham, R. W.; Keetle, S. F. A. *Inorg. Chim. Acta* **1970**, *4*, 145–149.

(23) Jezowska-Trzebiatowska, B.; Jezierska, J.; Baranowski, J.; Ozarowski, O. *J. Mol. Struct.* **1980**, *61*, 337–342.

(24) Baranowski, J.; Cukierda, T.; Jezowska-Trzebiatowska, B.; Kozlowski, H. *J. Magn. Res.* **1979**, *33*, 585–593.

(25) Syamal, A.; Theriot, I. J. *J. Coord. Chem.* **1973**, *2*, 241–242.

(26) Pauley, C. R.; Theriot, L. J. *Inorg. Chem.* **1974**, *13*, 2033–2035.

(27) Costes, J. P.; Serra, J. F.; Dahan, F.; Laurent, J. P. *Inorg. Chem.* **1986**, *25*, 2790–2795.

(28) Bencini, A.; Gatteschi, D. In *Magneto-structural correlations in exchange coupled systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1985; pp 241–268.

to the fact that the spin density along an equatorial bond which corresponds to the "doughnut" lobe of a z^2 type orbital is certainly smaller that along an axial bond, we can expect a reduction of the antiferromagnetic contribution in the two latter cases, i.e. for the couples Cu(201)/Cu(301), Cu(101)/Cu(201), and Cu(101)/Cu(401). As for the monoatomic bridge Cu(201)–O(202)–Cu(301), a literature survey[4,29] shows that it can only support a very weak antiferromagnetic interaction.

Those comments point out some factors that may be responsible for the lowering of the antiferromagnetic contribution. However they also underline the difficulty in analyzing, even at a qualitative level, the magnetic properties of a complex with a very distorted geometry.

Acknowledgment. R.K. is grateful to the Ella and Georg Hrnroth Foundation and the University of Granada for financial support. J.R. and E.C. are grateful to the Ministry of Education and Science for a grant and to the DGICYT for the project of investigation PB88-0482. We thank Dr. A. Mari for his contribution to the magnetic measurements.

Supplementary Material Available: Tables of ideal and observed angles for the polyhedra related to each copper atom and for the tetrahedron containing the four copper atoms, isotropic temperature factors for the O, N, C, and H atoms and anisotropic temperature factors for the copper atoms, fractional atomic coordinates for hydrogen atoms, and interatomic distances and bond angles (8 pages); structure factor tables (12 pages). Ordering information is given on any current masthead page.

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(29) Chiari, B.; Helms, J. H.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1986**, *25*, 870–874.

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The University of Mississippi, University, Mississippi 38677

Electrochemical and Spectroscopic Studies of Rhenium(IV) Monomeric and Dimeric Chloride Complexes in the Basic Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Room-Temperature Molten Salt

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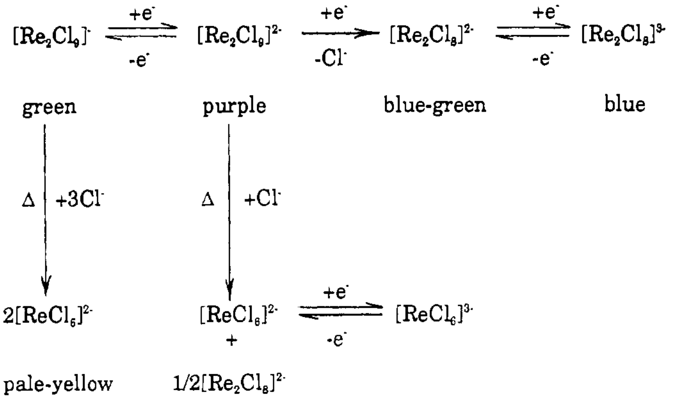
The monomeric rhenium(IV) chloride complex $[ReCl_6]^{2-}$ is stable in the basic aluminum chloride–1-methyl-3-ethylimidazolium chloride molten salt, and it can be reduced voltammetrically to $[ReCl_6]^{3-}$ at a glassy-carbon electrode in a reversible process with a half-wave potential of −0.87 V in the 49.0/51.0 mol % melt versus the Al^{3+}/Al couple in the 66.7/33.3 mol % melt. The Stokes–Einstein product for this complex is 2.3×10^{-10} g cm s^{-2} K^{-1}. The dimeric, metal–metal-bonded rhenium(IV) complex $[Re_2Cl_9]^-$ can be reduced voltammetrically to $[Re_2Cl_9]^{2-}$ in a reversible electrode reaction with a half-wave potential of approximately 0.56 V in the 49.0/51.0 mol % melt. However, $[Re_2Cl_9]^-$ exhibits only limited stability in the melt and slowly converts to $[ReCl_6]^{2-}$. The dimeric rhenium(IV,III) complex $[Re_2Cl_9]^{2-}$ can be reduced electrochemically to the dimeric rhenium(III) species $[Re_2Cl_8]^{2-}$ in an irreversible process. The Stokes–Einstein product for this complex is 1.6×10^{-10} g cm s^{-2} K^{-1}. Like $[Re_2Cl_9]^-$, $[Re_2Cl_9]^{2-}$ exhibits only limited stability in the melt; it slowly converts to a mixture of $[ReCl_6]^{2-}$ and $[Re_2Cl_8]^{2-}$. The conversion process is second order in $[Re_2Cl_9]^{2-}$ with a rate constant of 7.34×10^{-3} M^{-1} s^{-1} at 31 °C and an activation energy of approximately 92 kJ mol^{-1}. The overall chemical and electrochemical scheme for rhenium complexes in the basic $AlCl_3$–MeEtimCl molten salt is as follows:



Introduction

Room-temperature chloroaluminate molten salts or ionic liquids are obtained by combining aluminum chloride with certain quaternary ammonium chloride salts that are based on "bulky" cations like *N*-(*n*-butyl)pyridinium ($Bupy^+$) and 1-methyl-3-ethylimidazolium ($MeEtim^+$).[1] One very attractive feature of these chloroaluminate molten salts is their adjustable Lewis acidity, which can be varied over a very wide range by simply changing the relative proportion of aluminum chloride. Melts containing a molar excess of aluminum chloride are considered to be "acidic" because they contain one or more coordinately unsaturated, chloride ion acceptor species like $Al_2Cl_7^-$ and/or $Al_3Cl_{10}^-$. Conversely, melts formulated with a molar excess of the organic salt are designated as "basic" because they contain chloride ion

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(1) For reviews see: (a) Chum, H. L.; Osteryoung, R. A. In *Ionic Liquids*; Inman, D., Lovering, D. G., Eds.; Plenum: New York, 1981; pp 407–423. (b) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185–230. (c) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. 1, pp 55–78.

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