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Coordination Behavior of 4-Toluenesulfonamide Derivatives: Thermal, Magnetic, Spectroscopic, and Structural Properties of Bis(μ-*N*-tosylglycinato-*O*)bis(*N*-tosylglycinato-*O*)bis(2,2′-bipyridine)dicopper(II) Dihydrate

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Received June 13, 1984

The compound of formula $[Cu(TsGlyH)_2(bpy)]_2 \cdot H_2O$ (TsGlyH = *N*-tosylglycinate monoanion; tosyl = 4-toluenesulfonyl; bpy = 2,2′-bipyridine) was synthesized and characterized by means of structural, spectroscopic, thermal, and magnetic measurements. The compound crystallizes in the triclinic space group $P\bar{1}$ with 1 formula unit in a cell of dimensions a = 15.799 (2) Å, b = 10.337 (2) Å, c = 9.574 (2) Å, α = 87.88 (1)°, β = 102.01 (1)°, and γ = 80.41 (1)°. The structure was solved by Patterson and Fourier methods and refined by least-squares calculations to a conventional R factor of 3.22% for 3251 counter data. The structure consists of discrete dimeric units and uncoordinated water molecules. The coordination geometry at each copper center is distorted square pyramidal; the metal ions are bridged through monodentate carboxylate groups. The EPR and electronic data are consistent with the crystal structure. The EPR spectrum at 139 K shows the $\Delta M_s = 2$ transition characteristic of magnetically coupled binuclear copper(II) complexes. But, the very good linearity of the reciprocal molar susceptibility vs. temperature in the range 84–295 K suggests that only very weak exchange interactions may be present, consistent with a Cu–O–Cu angle of 100.0 (1)°. In the infrared spectrum the splitting of $\nu(OCO)_{as}$ is in accord with the different bonding modes of the carboxyl group.

Introduction

We have been interested for many years now in copper(II) N-protected amino acid complexes[1-4] as they could represent one of the simplest synthetic models for natural metalloenzymes.[5] Among these ligands, the most significant results have been obtained for *N*-tosylglycine[4] and *N*-tosyl-α-alanine[6] as their binding modes and active sites vary as a function of solvent and the pH of the media. Moreover, the ternary complexes of these latter ligands adopt coordination geometry dependent on the additional heterocyclic nitrogen organic base.[4d-f,6]

Since this class of ligands possesses the duo character of amino acid and sulfonamide derivatives, a further aim of our current investigation is a better understanding of the coordination behavior of sulfonamides.

In the present work we have synthesized a compound of empirical formula $[Cu(TsGlyH)_2(bpy)] \cdot H_2O$ (TsGlyH = *N*-tosylglycinate monoanion; tosyl = 4-toluenesulfonyl; bpy = 2,2′-bipyridine) that exhibits spectroscopic properties very different from those of structurally known simple and ternary copper(II) complexes with the *N*-tosylglycine monoanion[4c-e] as well as from the bis(*N*-tosyl-β-alaninato)(2,2′-bipyridine)copper(II), $[Cu(Ts\text{-}\beta\text{-}AlaH)_2(bpy)]$, complex.[7] These differences cannot be justified by the trivial statement that they are ascribed to a diffferent hydrogen-bonding network, and we thought it very probable that a new binding mode of *N*-tosylglycine may be present. In order to verify this, we report here the crystal and molecular structure and the spectroscopic, magnetic, and thermogravimetric analyses of this complex, and the results are discussed in comparison with those of the above cited complexes.

Table I. Summary of Crystal Data Collection

(A) Crystal Parameters[a] at 18 °C

cryst syst: triclinic
a = 15.799 (2) Å
b = 10.337 (2) Å
c = 9.574 (2) Å
V = 1503.8 Å^3
mol form: $C_{56}H_{60}Cu_2N_8O_9S_4$
ρ(calcd) = 1.53 g cm^{-3}
$F(000)$ = 718

space group: $P\bar{1}$ (C_i^1, No. 2)
α = 87.88 (1)°
β = 102.01 (1)°
γ = 80.41 (1)°
Z = 1
mol wt: 1388.48
ρ(obsd) = 1.51 g cm^{-3} (by flotation)

(B) Measurement of Data

radiation: graphite-monochromated Mo Kα (λ = 0.710 69 Å)
rflcns measd: $\pm h, \pm k, +l$
scan type: ω–2θ
θ range: 2–26°
scan speed: 3.0° min^{-1}
scan width: 1.2°
bkgd time: 10 s at beginning and end of the scan
std: 2 every 100 rflcns (no changes)
no. of collcd rflcns: 4693
no. of obsd rflcns: 3251 with $I > 3.0\sigma(I)$ [$\sigma(I)$ = (peak counts + total bkgd counts)$^{1/2}$]
cryst size: ~0.31 × 0.25 × 0.21 mm
abs coeff: 8.6 (abs cor not applied)

[a] Unit cell parameters and their esd's were derived from a least-squares fit to the setting angles of 24 automatically centered reflections (Mo Kα radiation).

Experimental Section

Preparation of $[Cu(TsGlyH)_2(bpy)]_2 \cdot 2H_2O$. Solid bpy was added to a water–methanol (2:1) solution of $[Cu(TsGlyH)_2 \cdot 4H_2O]$[4a] until a light blue solution was observed. By evaporation of the solution at ~20 °C, blue crystals separated. One of these crystals was selected for X-ray analysis. Anal. Calcd for $C_{56}H_{60}Cu_2N_8O_{18}S_4$: C, 48.42; H, 4.36; N, 8.07; S, 9.24; H_2O, 2.60. Found: C, 48.26; H, 4.43; N, 8.10; S, 9.11; H_2O, 2.69.

Physical Measurements. The electronic spectrum of the solid compound was recorded as a mull transmission spectrum with a Shimadzu MPS 50L spectrophotometer. The infrared spectrum was recorded with a Perkin-Elmer 180 spectrophotometer as KBr pellets and as a Nujol mull on KBr as support in the 4000–250-cm^{-1} spectral range. The EPR spectra were recorded with a Varian E-9 spectrometer equipped with X band (9 GHz) and an Oxford ESR 9 continuous-flow cryostat and with a Bruker ER 200D-SRC spectrometer.

Magnetic susceptibility measurements were obtained on a Newport Instruments magnetic (Gouy) balance employing a Newport Instruments cryostatic cooling system using $[HgCo(SCN)_4]$ as calibrant and were

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Table II. Final Positional Parameters[a]

atom	x	y	z
Cu	0.4550 (1)	0.0353 (1)	0.1389 (1)
N(1)	0.4448 (2)	0.1858 (3)	0.2619 (3)
C(1)	0.3843 (3)	0.2970 (4)	0.2302 (4)
C(2)	0.3801 (3)	0.3937 (4)	0.3242 (5)
C(3)	0.4387 (3)	0.3749 (4)	0.4549 (5)
C(4)	0.5012 (3)	0.2637 (4)	0.4873 (4)
C(5)	0.5042 (2)	0.1701 (3)	0.3880 (3)
N(2)	0.5626 (2)	−0.0262 (3)	0.2937 (3)
C(6)	0.6210 (2)	−0.1363 (4)	0.2965 (4)
C(7)	0.6891 (3)	−0.1779 (4)	0.4152 (5)
C(8)	0.6947 (3)	−0.1048 (5)	0.5324 (4)
C(9)	0.6350 (3)	0.0090 (4)	0.5298 (4)
C(10)	0.5700 (2)	0.0477 (3)	0.4070 (3)
O(1)	0.5242 (2)	0.1202 (2)	−0.0298 (2)
O(2)	0.5958 (2)	0.2197 (3)	−0.1647 (3)
C(11)	0.5636 (2)	0.2132 (3)	−0.0597 (4)
C(12)	0.5687 (3)	0.3149 (4)	0.0486 (4)
N(3)	0.6241 (2)	0.4076 (3)	0.0182 (3)
S(1)	0.6722 (1)	0.4798 (1)	0.1518 (1)
O(3)	0.7284 (2)	0.5533 (3)	0.0965 (3)
O(4)	0.6057 (2)	0.5458 (3)	0.2178 (3)
C(13)	0.7373 (2)	0.3544 (4)	0.2768 (4)
C(14)	0.8091 (3)	0.2772 (5)	0.2424 (5)
C(15)	0.8567 (3)	0.1747 (5)	0.3378 (5)
C(16)	0.8361 (3)	0.1485 (4)	0.4680 (4)
C(17)	0.7652 (3)	0.2268 (5)	0.4991 (5)
C(18)	0.7155 (3)	0.3282 (4)	0.4052 (5)
C(19)	0.8892 (4)	0.0354 (6)	0.5688 (7)
O(5)	0.3407 (2)	0.0911 (3)	0.0133 (3)
O(6)	0.2518 (2)	0.0200 (3)	0.1412 (3)
C(20)	0.2678 (2)	0.0636 (4)	0.0319 (4)
C(21)	0.1980 (3)	0.0880 (6)	−0.1064 (5)
N(4)	0.1112 (2)	0.0673 (4)	−0.0915 (4)
S(2)	0.0333 (1)	0.1935 (1)	−0.1058 (1)
O(7)	0.0345 (2)	0.2712 (4)	−0.2309 (4)
O(8)	−0.0443 (2)	0.1422 (3)	−0.0972 (4)
C(22)	0.0580 (2)	0.2830 (4)	0.0446 (5)
C(23)	0.0339 (3)	0.2485 (5)	0.1691 (6)
C(24)	0.0548 (4)	0.3144 (5)	0.2896 (6)
C(25)	0.1009 (3)	0.4164 (5)	0.2889 (8)
C(26)	0.1248 (4)	0.4492 (6)	0.1634 (10)
C(27)	0.1044 (3)	0.3848 (6)	0.0419 (8)
C(28)	0.1223 (6)	0.4892 (7)	0.4181 (10)
O(9)	0.7698 (2)	0.2750 (4)	0.8642 (4)

[a] The refined coordinates for 30 hydrogen atoms are given in supplementary material.

corrected for diamagnetism with the appropriate Pascal constants. Thermogravimetric analysis were performed at a speed rate of 5 °C/min with a Mettler TA3000 instrument.

X-ray Crystallography. The crystal selected for the X-ray analysis was sealed into a glass capillary and was directly mounted, in a random orientation, on a Philips PW 1100 automated four-circle diffractometer. All measurements were made at room temperature by using Mo Kα radiation, under the conditions listed in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption in view of the low absorption coefficient and small crystal size. Only the observed relfections, placed on an (approximately) absolute scale by means of a Wilson plot, were used in the structure analysis.

The centrosymmetric space group $P\bar{1}$ was initially assumed and then confirmed by the successful refinement of the structure, which was solved by conventional Patterson and Fourier techniques. Full-matrix least-squares refinement[8] of positional and anisotropic thermal parameters for all the non-hydrogen atoms and of positional parameters for hydrogen atoms (previously located in ΔF maps) led to final convergence at R = 3.22% and R_w = 3.33%. A final difference map was featureless, with no peaks higher than 0.25 e Å^{-3}. Unit weights were used at all stages, and no trend of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, sin θ, or Miller indices was observed. There was no evidence for secondary extinction.

Table III. Selected Interatomic Distances and Angles[a]

(a) Distances (Å)

Cu–N(1)	1.992 (3)	S(1)–O(3)	1.426 (4)
Cu–N(2)	2.002 (2)	S(1)–O(4)	1.428 (3)
Cu–O(1′)	1.968 (2)	S(1)–C(13)	1.760 (3)
Cu–O(5)	1.933 (2)	C(20)–O(5)	1.277 (5)
Cu–O(1)	2.350 (3)	C(20)–O(6)	1.214 (5)
Cu···Cu′	3.317 (1)	C(20)–C(21)	1.519 (5)
C(11)–O(1)	1.285 (5)	C(21)–N(4)	1.457 (6)
C(11)–O(2)	1.222 (5)	N(4)–S(2)	1.617 (4)
C(11)–C(12)	1.503 (5)	S(2)–O(7)	1.422 (4)
C(12)–N(3)	1.461 (6)	S(2)–O(8)	1.431 (3)
N(3)–S(1)	1.621 (3)	S(2)–C(22)	1.751 (5)

(b) Angles (deg)

N(1)–Cu–N(2)	80.9 (1)	O(1)–C(11)–O(2)	124.2 (3)
N(1)–Cu–O(1′)	174.6 (1)	O(1)–C(11)–C(12)	113.9 (3)
N(1)–Cu–O(5)	95.2 (1)	O(2)–C(11)–C(12)	121.9 (3)
N(1)–Cu–O(1)	100.2 (1)	C(11)–C(12)–N(3)	110.9 (3)
N(2)–Cu–O(1′)	93.7 (1)	C(12)–N(3)–S(1)	117.4 (3)
N(2)–Cu–O(5)	170.7 (1)	N(3)–S(1)–O(3)	106.1 (2)
N(2)–Cu–O(1)	97.8 (1)	N(3)–S(1)–O(4)	107.7 (2)
O(1′)–Cu–O(5)	90.1 (1)	N(3)–S(1)–C(13)	106.6 (2)
O(1′)–Cu–O(1)	80.0 (1)	O(3)–S(1)–O(4)	119.7 (2)
O(5)–Cu–O(1)	91.1 (1)	O(5)–C(20)–O(6)	127.8 (3)
Cu–O(1)–Cu′	100.0 (1)	O(5)–C(20)–C(21)	111.3 (4)
Cu–N(1)–C(1)	125.6 (2)	O(6)–C(20)–C(21)	120.9 (4)
Cu–N(1)–C(5)	115.0 (2)	C(20)–C(21)–N(4)	114.5 (4)
Cu–N(2)–C(6)	125.5 (2)	C(21)–N(4)–S(2)	118.9 (4)
Cu–N(2)–C(10)	114.6 (2)	N(4)–S(2)–O(7)	106.7 (2)
Cu–O(1′)–C(11′)	113.8 (2)	N(4)–S(2)–O(8)	106.0 (2)
Cu–O(5)–C(20)	126.6 (2)	N(4)–S(2)–C(22)	107.9 (2)
Cu–O(1)–C(11)	144.7 (2)	O(7)–S(2)–O(8)	119.2 (2)

[a] The primed atoms are related to unprimed by the symmetry transformation 1 − x, −y, −z of the reference coordinates.

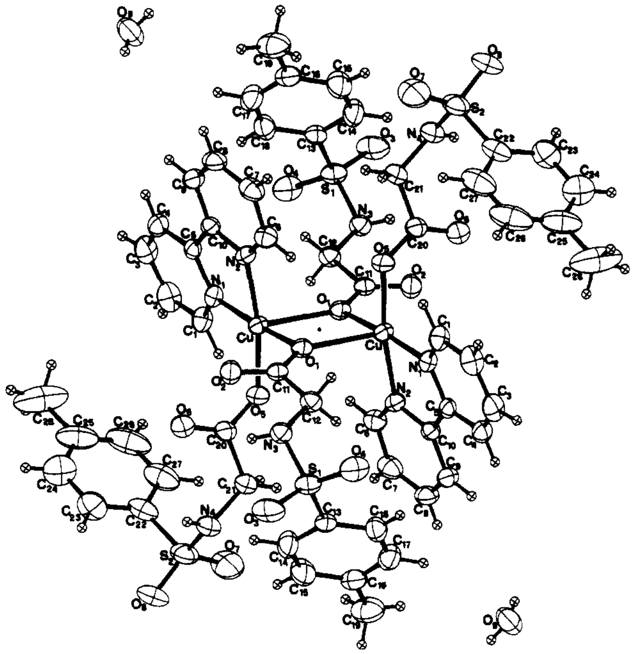

Figure 1. ORTEP view of [Cu(TsglyH)$_2$(bpy)]$_2$·2H$_2$O showing the numbering scheme and atomic vibrational ellipsoids (40%). The hydrogens are shown as spheres of arbitrary radius. Equivalent atoms are related by an inversion center.

Complex neutral-atom scattering factors[9a,b] were used throughout; major calculations were carried out on a CDC Cyber 7600 computer by using the SHELX 76 program package[10] and the ORTEP plotting program.[11] Final positional parameters for non-hydrogen atoms are given in Table II. Lists of anisotropic temperature factors, of hydrogen atom param-

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(8) The quantity minimized during refinement was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor. The unweighted and weighted residuals are defined as follows: $R = (\sum|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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eters, and of observed and calculated structure factors are available as supplementary material.

Analysis. Nitrogen, carbon, sulfur, and hydrogen were analyzed with a C. Erba elemental analyzer instrument, Model 1106, by G. Pistoni; the water content was determined gravimetrically by thermal analysis.

Results and Discussion

Description of the Structure. Selected interatomic distances and angles are reported in Table III, with atoms labeled as in Figure 1. Complete bond distances and bond angles, selected least-squares planes, and hydrogen-bonding interactions are given as supplementary material.

The structure consists of discrete dimeric $[Cu(TsGlyH)_2(bpy)]_2$ units and uncoordinated water molecules that provide crystalline stability through a network of hydrogen-bond interactions. The metal atoms of the complex binuclear molecule are bridged through two oxygens related by an inversion center (which requires the bridging Cu_2O_2 unit to be planar) in the middle of the dimer. Each copper ion shows distorted square-pyramidal geometry, the four basal ligands being two nitrogen atoms of the bpy ligand and two carboxyl oxygens from two unidentate TsGlyH ions, while the axial site is occupied by a carboxyl oxygen that is basal to the other copper center in the dimer.

The equatorial Cu–O(1′) bond length, only slightly longer than Cu–O(5), suggests that both are not markedly affected by the different bonding mode between O(1′) and O(5) *N*-tosylglycinate atoms.

The basal coordination plane is tetrahedrally distorted, with atomic deviations from the best fit plane ranging from −0.075 to 0.075 Å; the copper ion lies 0.072 Å above this plane in the direction of the apical atom. The closest approach to the sixth coordination site about the copper ion is due to the carboxylic O(2) atom, but the interatomic distance (2.897 (3) Å) and some interatomic angles (O(1)–Cu–O(2) = 49.8 (1)°) are out of the range of even weak coordination to the metal.[12] The coordinated distances are consistent with those previously reported for square-pyramidal copper(II) complexes.[4f,13-17] Only a few instances of metal bridging by monodentate carboxylate groups[14,15] have been observed: copper(II) (glycyl-L-hystidylglycine) hydrate, whose structure consists of five binuclear units;[18] copper(II) (4-toluidine)bis(propionato), with a linear chain structure determined by monoatomic and syn–syn carboxylate bridges;[19] tetraaquabis(μ-hippurato-*O*)bis(hippurato-*O*)dicopper(II) tetrahydrate $[Cu(Hippu)_2(H_2O)_4]_2$;[20,21] $[Cu(L)CH_3COO]_2 \cdot H_2O \cdot C_2H_5OH$ (LH = *N*-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine),[22] where the two copper atoms are connected by a single-atom bridge through the acetate oxygen.

The dimensions of the coordination polyhedron of our complex closely parallel those of the hippurate derivative,[20,21] with very similar values of bond distances, Cu···Cu separation (3.317 (1) vs. 3.33 Å), and Cu–O–Cu bridging angle (100.0 (1) vs. 101.0°). It is also interesting to note that in both complexes the anionic ligands (glycine derivatives in both cases) exhibit the same metal binding, acting either as simple monodentate or as monodentate bridging, through carboxyl oxygens. Furthermore, the C–O bond distances for coordinated O atoms (average 1.281 (5) Å) are significantly longer than those for uncoordinated O atoms (average 1.218 (5) Å); their values compare well with those reported for the hippurate derivative (1.29 and 1.21 Å, respectively). We also observe that the four equatorial bond distances and angles of our complex are very close to those of the cited square-planar monomeric $[Cu(Ts\text{-}\beta\text{-}AlaH)_2(bpy)]$ complex[7] where the *N*-tosyl-β-alaninate anion acts only as unidentate carboxylate ligand.

Table IV. Room-Temperature (298 K) Electronic ($\times 10^{-3}$ cm^{-1}), Infrared (cm^{-1}), EPR and Magnetic Moment[a] (μ_B), and Low-Temperature EPR (4.2 and 139 K) and Magnetic Moment (84 K) Results, Weight-Loss Temperature Range (K), and Decomposition Temperature (K) for $[Cu(TsGlyH)_2(bpy)]_2 \cdot 2H_2O$

wt loss temp range	353–413	$\nu(OH)_{as}$	3580 s
dec temp	433	$\nu(OH)_s$	3490 ms
μ_{eff}(295 K)	1.938	$\nu(NH)$	3290 ms, 3250 m
μ_{eff}(84 K)	1.955	$\nu(OCO)_{as}$	1650 vs, 1600 vs
$g_{\parallel}$(4.2 K)	2.27	$\nu(OCO)_s$	1370 vsb
$g_{\parallel}$(139 and 298 K)	2.28	$\nu(SO_2)_{as}$	1320, 1310 vs
$g_{\perp}$(4.2, 139, and 298 K)	2.08	$\nu(SO_2)_s$	1160 vs
$\langle g \rangle$[b]	2.15	$\nu(SN)$	900 ms
d–d band max	16.3		
CT band	26.3 sh		

[a] $\mu_B = 0.92732 \times 10^{-20}$ erg/G. [b] $g = [(g_{\parallel} + 2g_{\perp})/3]$.

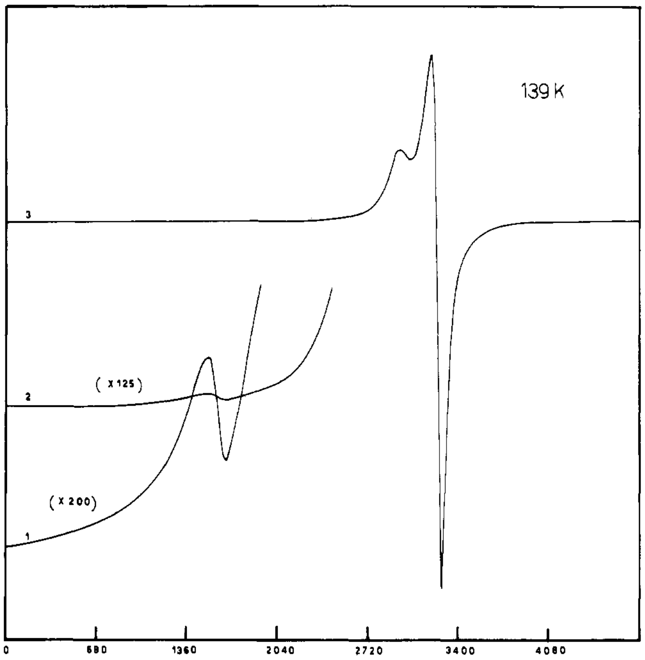

Figure 2. EPR spectrum of $[Cu(TsglyH)_2(bpy)]_2 \cdot 2H_2O$ at 139 K.

Bond distances and bond angles within the TsGlyH ligands are normal and consistent with those previously observed in other copper complexes of the same monoanion.[4c-e]

The dimensions of the bpy molecule, whose individual pyridine rings, planar within ±0.016 Å, are twisted by 5.0° about the 2,2′ bond, compare well with those previously reported for this coordinated ligand.[7,16,23]

The crystal packing is mainly determined by a tridimensional network of hydrogen-bonding interactions that involve amino or water H atoms and uncoordinated carboxyl or sulfonic O atoms. The N···O or O···O separations range from 2.860 to 3.140 Å, and the angles at the involved H atoms, from 167 to 126°.

Thermogravimetric, Magnetic, and Spectroscopic Results. The thermogravimetric analysis shows that the loss of water begins at a relatively high temperature, the water molecule being involved in three hydrogen bondings.

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Magnetic susceptibility measurements of polycrystalline samples between 84 and 295 K strictly obey the Curie-Weiss law of the form (1), where $Ng^2\beta^2/4k = C$, χ_M is the molar susceptibility

$$\chi_M = \frac{Ng^2\beta^2}{4k(T - \Theta)} + N\alpha \quad (1)$$

corrected for diamagnetism (-716.6×10^{-6} cgsu), $N\alpha$ is the temperature-independent paramagnetism (TIP = 120×10^{-6} cgsu for the dimer molecule).

A least-squares fit of the reciprocal of molar susceptibility, corrected for both the diamagnetism and temperature-independent paramagnetism, vs. temperature according to the equation (1) gives a C value of 2.271 cgsu, $\Theta = 7.2$ K, and $g = 2.16$ in agreement with the average value of 2.15 obtained from EPR spectra (Table IV). The EPR spectra at different temperatures (4, 139, 298 K) are very similar to one another, are of the axial type, and show a sharp maximum in the 3000-G spectral region, while a further low-field resonance corresponding to $\Delta M_s = 2$ is present in the spectrum at 139 K (Figure 2). This transition indicates the presence of magnetically coupled copper(II) ions within each dimer,[24] but the very good agreement of magnetic data down to 84 K with eq 1 suggests that exchange interactions allow only for a very small $|2J|$ value, in agreement with the reported value for the structurally analoguous $[Cu(Hippu)_2(H_2O)_4]_2$ ($|2J| = 4.3$ cm^{-1} [25]), attributable to the quasi-orthogonality between the s and p orbitals on the bridging oxygen and the orbital on one copper that contains the unpaired spin (Cu-O-Cu = 100.0 (1)° in the present complex and 101.0° in the hippurato complex).

The EPR and electronic parameters (Table IV) are similar to those of square-pyramidal copper(II) complexes with the CuN_2O_3 chromophore,[26] and comparison with the spectroscopic data of $[Cu(Hippu)_2(H_2O)_4]_2$ (d-d band maxima: 680 and 880 nm,[20] 685 and 900 sh nm,[27] $g_\parallel = 2.356$ and $g_\perp = 2.068$[28]) reveals the expected displacement of d-d band maxima to greater energy and that of g parameters to lower values because of the chromophore change from CuO_5 in the hippurate derivative to CuN_2O_3 in tosylglycinate.

In the infrared spectrum (Table IV), the absorption frequencies of the uncoordinated functional groups (NH, SO_2) are in the range found for the other copper(II)-*N*-tosylglycinate monoanion complexes[4] and for $[Cu(Ts\text{-}\beta\text{-}AlaH)_2(bpy)]$[7] except for the polymeric $[Cu(TsGlyH)_2]_n$, which shows one sulfonic oxygen coordinated to the copper atom[4c]). The only significant difference among the infrared spectra of the present and of previously cited complexes concerns the splitting of the absorption frequencis of the carboxylate group as a consequence of the different bonding modes in which this group is involved in the present complex. The asymmetric stretching band at 1650 cm^{-1} is assigned to the bridging carboxyl group and that at 1600 cm^{-1} to the monodentate carboxyl group; a broad unresolved band assignable to the symmetric stretching of both carboxyl groups is found at 1370 cm^{-1}. In Table IV we also report the bands attributable to the water molecule.

Acknowledgment. The authors are grateful to the Centro di Calcolo Elettronico dell'Università di Modena for computing support, the Centro Strumenti dell'Università di Modena for recording the infrared spectra, Prof. A. Vacca of ISSECC, CNR, Florence, Italy, for allowing the use of EPR spectrometers, and Prof. G. C. Pellacani for helpful discussions.

Registry No. $[Cu(TsglyH)_2(bpy)]_2 \cdot 2H_2O$, 94203-47-1; $[Cu(TsglyH)_2(bpy)]_2 \cdot 4H_2O$, 94292-15-6.

Supplementary Material Available: Lists of observed and calculated structure factors, atomic temperature factors, hydrogen atom parameters, complete bond distances and bond angles, hydrogen bonding distances and angles, selected least-squares planes, and experimental and calculated corrected molar susceptibilities and magnetic moments (27 pages). Ordering information is given on any current masthead page.

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Intercalation of Niobium and Tantalum $M_6Cl_{12}{}^{n+}$ Cluster Cations in Montmorillonite: A New Route to Pillared Clays

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Received July 9, 1984

A new synthetic route to pillared clays is described that is based on the intercalation and subsequent oxidation of metal cluster cations in montmorillonite. Niobium and tantalum clusters of the type $M_6Cl_{12}{}^{n+}$ (n = 2, 3) are shown to bind to the clay by ion exchange for interlayer sodium. The maximum cluster loading is larger than expected on the basis of formal cation charge and clay ion-exchange capacity, indicating that reduction of cluster charge occurs through hydrolysis on the intracrystal surfaces. The intercalated products exhibit regular basal spacings of 18.4 ± 0.2 Å (M = Nb) and 18.9 ± 0.5 Å (M = Ta). Oxidation of the intercalated cluster cations by water at 240 °C results in the in situ formation of metal oxide aggregates that function as molecular size pillars. The niobium and tantalum oxide pillared clays exhibit basal spacings of 19.9 ± 0.5 Å and are thermally stable to 400 °C.

Introduction

Pillared clays are smectite clay minerals that have been modified through the introduction of robust cations into their interlayer regions. The intercalated cations function as molecular props or pillars between the silicate layers, creating a highly porous structure with a large intracrystalline surface area suitable for molecular absorption and catalysis. Early pillaring experiments by Barrer and co-workers[1,2] dealt with the intercalation of alkylammonium ions in montmorillonite. These bulky cations propped the silicate sheets apart by 4.0-4.5 Å and markedly improved the diffusive and sorbtive properties of the host silicate. Later work by Shabtai et al.[3] and by Berkheiser and Mortland[4] utilized the sterically rigid protonated dication of 1,4-diazabicyclo[2.2.2]octane to achieve an interlayer free spacing of approximately 5 Å. The alkylammonium pillared clays, however, were

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