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Carboxysilanes and -germanes. 5.[1] Copper(II) Complexes of Carboxysilanes and -germanes: Structure and Magnetic Properties. Crystal Structure of Tetrakis(μ-phenyldimethylsilanecarboxylato)bis[aquocopper(II)][2]

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Copper(II) complexes of carboxysilanes and -germanes have unusually small magnetic moments at ambient temperature. A singlet–triplet energy separation, $|-2J| = 1000 \pm 150$ cm^{-1}, determined by variable-temperature ESR studies on three complexes, $[Cu(O_2CSiR_3)_2\cdot H_2O]_2$ (R = Ph, Me), is much larger than has been reported previously for copper(II) carboxylates. The structure of $[Cu(O_2CSiPhMe_2)_2\cdot H_2O]_2$ has been determined to be of the copper(II) acetate monohydrate type, which crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 14.067$ (6) Å, $b = 11.952$ (3) Å, $c = 14.147$ (9) Å, $\alpha = 90.33$ (4)°, $\beta = 130.80$ (4)°, and $\gamma = 68.91$ (2)°. Structural refinement led to the introduction of two conformers (1:1) that differ by rotation about trans Si–C bonds. The $Cu_2(CO_2)_4$ cage shows considerable distortion from D_{4h} symmetry. Magnetic susceptibility studies, molecular weight determinations, and ^{1}H NMR studies all indicate that the dimer structure is maintained in solution. The enhanced exchange coupling in the copper(II) complexes of carboxysilanes and -germanes is explained in terms of σ and π interactions between the metalloid and the carboxylate group.

Introduction

Since Bleaney and Bowers, in 1952, proposed magnetic exchange coupling between a pair of copper(II) atoms in copper(II) acetate monohydrate on the basis of ESR studies[5a] and van Niekerk and Schoening, in 1953, found a binuclear structure for copper(II) acetate monohydrate involving bridging acetate groups and a short Cu–Cu distance,[5b] numerous studies have been carried out to investigate the nature of the interaction between the two copper centers.[6] In this paper, we report the preparation and magnetic properties of dimeric copper(II) carboxylates with bridging triorganosilanecarboxylate and triorganogermanecarboxylate ligands that greatly enhance the coupling.[1,2]

The structure of one of the complexes, $Cu(O_2CSiPhMe_2)_2\cdot H_2O$, was determined by X-ray diffraction, since it was necessary to show that these complexes have the same type of structure as copper(II) acetate monohydrate.

At the same time, copper(II) has been used as a probe to investigate the interaction between the carboxylate groups and the metalloid in the ligand. Previously, we have reported studies on the acidity of carboxysilanes and -germanes that suggest that the enhanced acidity over their carbon analogues is due to greater charge delocalization in the anion.[1,7-9]

Experimental Section

General Procedures. All calculations for copper(II) carboxylate are based on formula weights. Analyses were performed by Alfred Bernhardt Microanalytical Laboratories, Elbach, West Germany, with the exception of some copper analyses that were performed in our laboratory using an EDTA-titration method.

Materials. The starting materials (and sources) are as follows: benzene-d_6 (99.5 atom % D), acetone-d_6 (99.5 atom % D), diphenylmethylacetic acid, triphenylacetic acid (Aldrich Chemical Co.); phenyldimethylacetic acid (ICN Pharmaceuticals); copper(II) perchlorate hexahydrate (Alfa Products, Ventron Corp.); copper(II) acetate monohydrate, zinc acetate dihydrate (Fisher Scientific Co.).

Triphenylsilanecarboxylic acid, diphenylmethylsilanecarboxylic acid, phenyldimethylsilanecarboxylic acid, and triphenylgermanecarboxylic acid were synthesized by reported procedures;[7,10,11] their physical properties have been reported.[7]

Preparation of the Complexes. Detailed descriptions of the synthetic procedures used are given below by citing typical examples. Generally, yields are >90%. The preparative method and analytical data for each complex are listed in supplementary table I-S.

(a) $M'(O_2CMR_3)_2\cdot H_2O$ (M′ = Cu, Zn; M = Si, Ge): Procedure 1. Triphenylsilanecarboxylic acid (1.25 g, 4.11 mmol) was dissolved in 95% ethanol (100 mL), and copper(II) acetate monohydrate (0.41 g, 2.06 mmol) was dissolved in distilled water (50 mL). After filtration, the copper(II) acetate solution was slowly added with stirring to the acid solution. A green precipitate formed immediately. After the mixture was allowed to stand for 15 min, the precipitate was collected in a Büchner funnel with a fritted disk (reduced-pressure filtration). The precipitate was washed with 75% ethanol–25% water (100 mL) and air-dried for 2 days, giving 1.30 g, 1.98 mmol (91.7% yield), of $Cu(O_2CSiPh_3)_2\cdot H_2O$.

Since the solubility of the complexes increases with the number of methyl groups in the ligand, the ethanol content of the wash solution should be reduced accordingly (Ph_2MeSi, 50% EtOH–50% H_2O; $PhMe_2Si$, H_2O).

(b) $Cu(O_2CCR_3)_2\cdot nH_2O$: Procedure 2. Triphenylacetic acid (3.50 g, 12.1 mmol) was dissolved in 0.25 N sodium hydroxide (100 mL, 25.0 mmol), and the resulting cloudy solution was filtered. Phenolphthalein (2 drops) was added to the solution, and 1.0 M nitric acid was added from a buret until the end point was reached. Copper(II) perchlorate hexahydrate (3.30 g, 12.1 mmol), dissolved in water (50 mL), was added to the above solution. A blue-green precipitate formed immediately. After filtration (Büchner funnel with fritted disk), the precipitate was extracted several times with 50% ethanol–50% water, 200 mL total volume, to remove unreacted acid. After being washed with water (50 mL), the precipitate was allowed to air-dry for 2 days, yielding 4.02 g, 5.96 mmol (98.5% yield), of $Cu(O_2CCPh_3)_2\cdot 2H_2O$.

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Table I. Crystallographic Data for $Cu_2(O_2CSiPhMe_2)_4{\cdot}2H_2O$

mol wt	824.03	ρ_c, g/cm^3	1.27
space group	$P\bar{1}$	μ, cm^{-1}	26.8
a, Å	14.067 (6)	no. of data	8287
b, Å	11.952 (3)	no. of unique data	6696
c, Å	14.147 (9)	no. of data with $I \geq 3\sigma(I)$	3060
α, deg	90.33 (4)	no. of variables	734
β, deg	103.80 (4)	R	0.076
γ, deg	68.91 (2)	R_w	0.102
V, Å^3	2146.59		
Z	2		

For compounds with fewer phenyl groups, see the comment at the end of procedure 1.

(c) $Cu(O_2CMR_3)_2{\cdot}nL$ (M = C, Si, Ge; nL = Me_2SO, py, 2 Aniline): Procedure 3. $Cu(O_2CGePh_3)_2{\cdot}H_2O$ (0.92 g, 1.18 mmol) was dissolved in benzene (120 mL), yielding a purple solution. Warming on a steam bath reduces the time required for the complex to dissolve. After filtration, pyridine (0.60 g, 7.59 mmol) was added, resulting in a color change, purple to dark green. The complex was precipitated by adding petroleum ether, bp 30–60 °C (300 mL). After filtration (Büchner funnel with fritted disk), the precipitate was washed with 30% benzene–70% petroleum ether and allowed to air-dry, yielding 0.94 g, 1.12 mmol (94.9% yield), of $Cu(O_2CGePh_3)_2{\cdot}py$.

The greater solubility of the compounds with methyl substituent groups in the ligand requires a reduction in the amount of benzene or precipitation will not occur (Ph_2MeSi, 25% benzene–75% petroleum ether; $PhMe_2Si$, 10% benzene–90% petroleum ether; wash, petroleum ether).

Crystal Preparation. Crystals of $Cu(O_2CSiPhMe_2)_2{\cdot}H_2O$ were obtained by a solvent diffusion method. $Cu(O_2CSiPhMe_2)_2{\cdot}H_2O$ (0.5 g, 1.2 mmol) dissolved in 1,2-dimethoxyethane (20 mL) was placed in a small beaker in a desiccator. Distilled water was placed in the bottom of the desiccator. Green crystals (needles) formed in the beaker during refrigeration for 14 days at ~4 °C.

X-ray Procedures. (a) Collection and Reduction of the Data. The crystal selected had the dimensions 0.15 × 0.25 × 0.50 mm, the longest along the c axis of the unit cell. Rotation photographs taken along the c axis showed that there were alternative strong and weak layer lines. Weissenberg photographs of the weak lines consisted of mostly diffused reflections; this is evidence of disorder. The crystallographic data for the compound are given in Table I. The triclinic unit cell was first determined from the Weissenberg photographs and refined by a least-squares fit of the orientation and 2θ angles for 12 reflections measured on the diffractometer. The space group, $P\bar{1}$, was assumed and confirmed by successful refinement of the structure. Intensity data were collected at room temperature with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) on a Picker FACS-1, X-ray diffractometer to a 2θ limit of 127°. The 6696 independent reflections were measured by the θ–2θ scan technique over a scan range of 2° at a scan rate of 1°/min. The background was counted for 20 s at each end of the scan range. Three standard reflections were monitored after each 100 reflections; their intensities decreased by less than 5%. The intensities were converted to relative structure amplitudes after correction for Lorentz and polarization effects appropriate for graphite-monochromated radiation ($2\theta_m$ = 26.40°). Since the extended cell was used for collecting data, only a few of the l-odd reflections were qualified as observed reflections ($|F| \geq 6\sigma(F)$); therefore, over half of the total reflections with $2\theta < 127°$ were unobserved.

(b) Solution and Refinement of the Crystal Structure. The copper positions were determined by using the subcell c = 7.074 Å. The Fourier map, which was synthesized by using the copper positions, showed the adjacent oxygen positions. By reiteration, the positions of the carboxyl groups, the silicon atoms, and some of the methyl and phenyl groups were located. The R factor was reduced to 0.25 wtih isotropic temperature factors.

When it became evident that further refinement was not possible, the extended cell, c = 14.147 Å, was used. Anisotropic temperature factors were assigned, the $P\bar{1}$ space group was used, and the center of inversion was placed between two molecules. Due to the large number of atoms in the unit cell, the least-squares refinements were carried out by blocking the atoms into several groups. The refinements up to this point were carried out by using the AP program QWKREF.[12] The quantity $\langle w(F_o - F_c)^2\rangle$ was minimized, where $w^{-1} = \sigma^2(F)$. With R = 0.14, a phenyl group had not been located and some abnormal distances and angles were obtained.

Since further improvement was not possible, the rigid-body method was employed by using the program SHELX-76.[13] A Fourier map was calculated after removal of all atoms having questionable positions. Rigid and ideal benzene rings were positioned as indicated by the Fourier map. Cycles of refinement were carried out by SHELX-76, followed by QWKREF. The final location of atoms was adopted that gave the lowest R factor, 0.076, and reasonable bond distances and angles.

Magnetic Susceptibility Measurements. Magnetic susceptibilities (microcrystalline solids) were measured by Faraday[14,15] (instrument built at Carnegie-Mellon University using Varian components) and Gouy[14–16] (Ainsworth balance; General Electric Isthmus electromagnet, 75 V, 10 A; Alpha Model 7500PS power supply) methods at several different field strengths. Platinum wire was used as a calibrant for the Faraday method (χ_g taken as 0.936 × 10^{-6} cgsu at 25 °C); the calibrants employed for the Gouy method were $Ni(en)_3S_2O_3$ (χ_g taken as 11.03 × 10^{-6} cgsu at 20 °C, decreasing by 0.04 × 10^{-6} cgsu per degree temperature rise), $HgCo(NCS)_4$ (χ_g taken as 16.44 × 10^{-6} cgsu at 20 °C, decreasing by 0.05 × 10^{-6} cgsu per degree temperature rise), and deoxygenated deionized water (χ_g taken as −0.720 × 10^{-6} cgsu, increasing by 0.0009 × 10^{-6} cgsu per degree rise near 20 °C). Pascal's constants[14–16] were used to correct for the diamagnetism of constituent atoms.

Magnetic susceptibilities for the compound in solution were determined by the Evans method[17] using a Perkin-Elmer R-600 FT NMR spectrometer. The copper(II) carboxylate, 1 × 10^{-6}–1 × 10^{-5} mol, was dissolved in 1 mL of benzene-d_6 containing 0.02 mL of cyclohexane. This solution was placed in a 1.6 mm o.d. capillary that was inserted into a 5 mm o.d. glass NMR tube with Teflon holders, containing 1 mL of the above solvent. At least three high-resolution scans were run, 50 Hz full scale, at 35 °C. The paramagnetic contribution to the magnetic susceptibility was calculated from the frequency separation of the two lines with correction for the diamagnetism of the solvent (χ_g taken as −0.702 × 10^{-6} cgsu at 35 °C[18]).

The effective magnetic moments, μ_{eff}, were calculated by using the equation, $\mu_{eff} = 2.83[(\chi'_M - N\alpha)T]^{1/2}$, where $N\alpha$ represents the temperature-independent paramagnetism associated with the copper(II) ($N\alpha$ was taken as 60 × 10^{-6} cgsu[19]) and χ'_M is the magnetic susceptibility per mole of metal ion corrected for diamagnetism.

Electron Spin Resonance Measurements. The ESR spectra were obtained from powdered samples in quartz tubes on a Varian E-4 X-band spectrometer with a variable-temperature controller. Typical instrument settings were 100-kHz modulation frequency, 50–200-mW microwave power, 9.09-GHz microwave frequency. A sample of DPPH was used as an external standard (g = 2.0037).

Molecular Weight Determinations. Molecular weight data were obtained with Mechrolab, Model 301A, and Knauer vapor-phase osmometers at 37 °C. Benzil in THF and benzene was used to calibrate the instruments. Benzene (Fisher Spectroanalyzed grade) was used without further purification, and THF (Fisher Certified reagent grade) was distilled from calcium hydride. No attempt was made to keep the solvents dry since the aquo complexes were being used. The concentrations employed are reported in Table V.

Results

Structure. The crystal structure of bis(phenyldimethylsilanecarboxylato)aquocopper(II) is composed of dimeric units of the copper(II) acetate monohydrate type. Refinement of the structure, using the rigid-body method, led to the introduction of two conformers in a 1:1 ratio. The atomic positional and isotropic thermal parameters are listed in Table II. The molecular structures of the two conformers **1** and **2** are depicted in Figures 1 and 2, respectively. Some important bond lengths and angles are given in Table III.

Conformers **1** and **2** differ by rotations of ca. 30° about the Si(1)–C(11) and Si(3)–C(31) bonds with concurrent rotations about the Si–Ph bonds. Short intermolecular distances, <3.00

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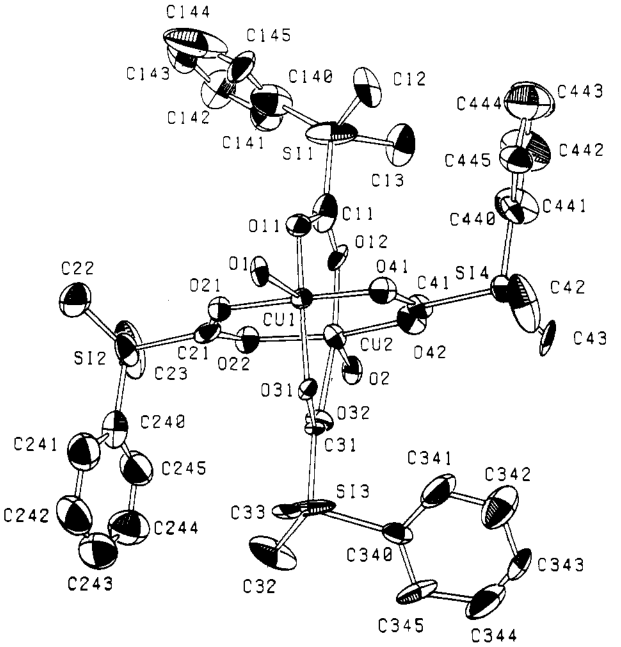

Figure 1. Molecular structure of $[Cu(O_2CSiPhMe_2)_2 \cdot H_2O]_2$, conformer **1**. Thermal elliposids are drawn to the 50% probability level.

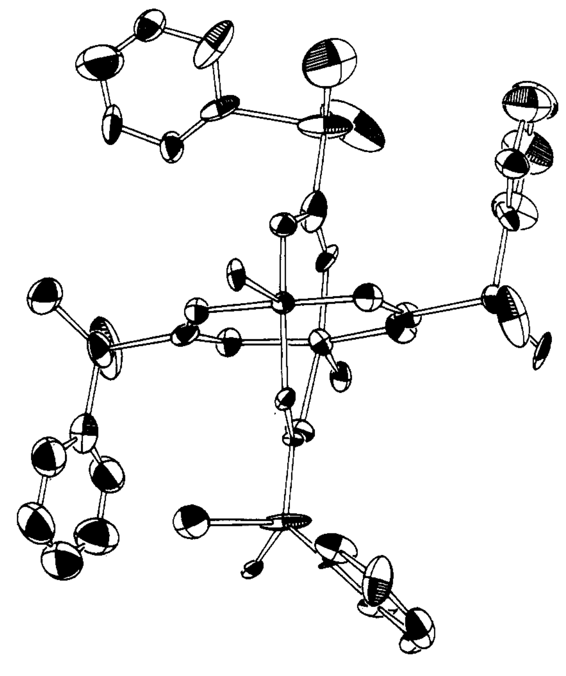

Figure 2. Molecular structure of $[Cu(O_2CSiPhMe_2)_2 \cdot H_2O]_2$, conformer **2**. Thermal elliposids are drawn to the 50% probability level.

Å, between conformers **1** and **2**, most of which are less than the sum of the van der Waals radii, are given in Table III-S (supplementary material). The intermolecular distances in conjunction with the diffraction data (cf. X-ray Procedures) suggest that the conformers occur in different regions of the crystal and the regional conformation is determined by chance.

Only one $Cu_2(CO_2)_4$ cage structure, which is well-defined by the crystallographic data, is observed for the two conformers. The $Cu_2(CO_2)_4$ cage shows considerably more distortion from D_{4h} symmetry than has been reported previously,[6] with the exceptions of two recently reported structures in which the copper atoms approach a trigonal-bipyramidal arrangement.[20] This distortion most likely arises from intermolecular interference in the crystal due to the bulky nature of the phenyldimethylsilyl group.[23] The Cu–Cu distance, 2.578 (1) Å, while shorter than observed for copper(II) acetate monohydrate, is comparable to the distances reported for a number of copper(II) carboxylates of similar structure; cf. Table VII. The carboxylate bridges between the two crystallographically independent copper atoms are all of different lengths (6.37–7.02 Å); the average length, 6.63 Å, is greater than the reported values for structures of this type.[6] The longest bridges are adjacent.

Interestingly, the copper–basal plane distances are different (0.13 and 0.22 Å), the former being considerably shorter than previously observed.[6] The apical Cu–O distances (aquo ligands) also are different (2.08 and 2.30 Å); the longer copper–apical ligand distance corresponds with the shorter copper–basal plane distance. The apical aquo ligands form an angle of ca. 173° with the Cu–Cu bond.

Magnetic Susceptibility. We have observed that the magnetic properties of copper(II) salts of carboxysilanes and -germanes are quite different from those of their carbon analogues (for preliminary reports, cf. ref 2). The complexes $Cu(O_2CMR_3)_2 \cdot nL$ (M = Si, Ge; L = H_2O, Me_2SO, py, aniline) although diamagnetic overall, exhibit magnetic moments that are much smaller than any previously reported moments for dimeric copper(II) alkanoates, while the moments of the carbon analogues are consistent with previous studies;[6,19] cf. Table IV. These observations are particularly significant since they allow us to obtain a better understanding of the factors involved in the magnetic exchange coupling in dimeric copper(II) carboxylates.

The magnetic susceptibilities were determined by three methods, Faraday, Gouy, and Evans, and are consistent within experimental error. The Faraday method is generally more accurate than the Gouy method owing to better balance sensitivity and the elimination of errors due to packing. Small magnetic moments as observed for the copper(II) complexes of carboxysilanes and -germanes are susceptible to unavoidably large errors resulting from the diamagnetic corrections for large ligands and trace amounts of paramagnetic impurities. The Evans method[17] gives only the paramagnetic contribution to the magnetic moment. The results of these studies on benzene-d_6 solutions of the complexes show that the dimeric structure is maintained in this solvent (cf. Solution Properties).

A general trend is observed between the magnetic moment and the +*I* effect of R in $R_3MCO_2^-$: the magnetic moment decreases as substituent phenyl groups are replaced by methyl groups.[24] For the effect of substituting silicon or germanium for an α-carbon, cf. the Discussion.

It should be pointed out that the magnetic susceptibility data on the complex $Cu(O_2CGePh_3)_2 \cdot 2C_6H_5NH_2$ are consistent with a dimer-type structure. This observation is noted because of the work of Doedens,[6] which shows that the structure of an aniline complex is a function of the coordinated carboxylate ligand.

Solution Properties. The complexes $Cu(O_2CMR_3)_2 \cdot nH_2O$ (M = Si, Ge) undergo a striking color change on dissolving in benzene, dark green to purple; the carbon analogues undergo a more subtle change in color, blue-green to blue. Similar reversible color changes occur when the solids are placed under vacuum in a desiccator. However, if an electron-donor solvent is used, such as THF, ether, or alcohol, the colors of the solids are retained in

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(20) The structures of $[Cu(O_2CCPh_3)_2 \cdot py \cdot 0.5C_6H_6]_2$[21] and $[Cu(O_2CCCl_3)_2 \cdot tempo]_2$[22] have four bridging carboxylate ligands, of which two adjacent bridges are long and asymmetric; there is one long Cu–O bond to each copper atom.

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Table II. Positional and Isotropic Thermal Parameters (×10^4) and Their Standard Deviations for $Cu_2(O_2CSiPhMe_2)_4 \cdot 2H_2O$[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2	atom	*x*	*y*	*z*	B_{eq}, Å^2
Cu(1)	9993 (1)	506 (1)	1727 (1)	1.8	C(443)	4490 (14)	3173 (16)	1455 (15)	7.1
Cu(2)	9844 (1)	−431 (1)	3295 (1)	2.2	C(444)	4692 (15)	3115 (15)	542 (14)	7.1
O(11)	9235 (5)	1955 (6)	2103 (5)	2.8	C(445)	5495 (10)	2069 (11)	375 (9)	3.9
O(12)	8930 (5)	1119 (6)	3406 (5)	2.5	C(12)′	7018 (54)	4785 (46)	1650 (50)	10.8
O(21)	11255 (5)	742 (6)	2592 (5)	2.3	C(13)′	7221 (30)	3523 (42)	4028 (24)	9.8
O(22)	11137 (5)	−21 (6)	3977 (5)	2.6	C(140)′	8967 (22)	4460 (19)	3394 (17)	3.9
O(31)	10879 (5)	−1272 (5)	1511 (5)	2.0	C(141)′	10026 (18)	3936 (22)	3839 (21)	4.5
O(32)	10993 (5)	−1991 (6)	2991 (5)	2.7	C(142)′	10638 (22)	4632 (28)	3908 (30)	6.2
O(41)	8778 (6)	232 (6)	1046 (5)	2.9	C(143)′	10210 (36)	5843 (32)	3514 (38)	10.3
O(42)	8586 (6)	−516 (7)	2444 (5)	3.1	C(144)′	9141 (21)	6342 (22)	3271 (18)	4.1
O(1)	10362 (5)	1257 (6)	421 (4)	2.2	C(145)′	8423 (40)	5696 (39)	3035 (28)	6.4
O(2)	9901 (5)	−1235 (6)	4618 (5)	2.7	C(32)′	12993 (25)	−4347 (33)	3203 (39)	4.2
C(11)	8670 (10)	2066 (12)	2940 (9)	4.0	C(33)′	13312 (21)	−3093 (23)	1721 (21)	4.3
C(21)	11657 (9)	342 (8)	3392 (9)	3.1	C(340)′	11812 (14)	−4451 (13)	1173 (12)	1.5
C(31)	11163 (6)	−2078 (7)	2226 (6)	1.1	C(341)′	11591 (19)	−4150 (21)	147 (15)	3.6
C(41)	8388 (8)	−277 (9)	1458 (6)	2.4	C(342)′	11336 (25)	−4879 (30)	−581 (21)	5.7
Si(1)	7667 (4)	3639 (3)	3037 (3)	5.7	C(343)′	11212 (20)	−5957 (28)	−153 (24)	5.4
Si(2)	12993 (2)	433 (3)	4221 (2)	3.6	C(344)′	11367 (22)	−6236 (21)	818 (21)	4.7
Si(3)	12065 (4)	−3557 (3)	2010 (3)	4.6	C(345)′	11611 (24)	−5523 (26)	1496 (23)	4.8
Si(4)	7046 (2)	−363 (3)	875 (2)	2.7	H(141)	8200	3761	5142	4.7
C(12)	6748 (42)	4299 (58)	1651 (32)	4.5	H(142)	8886	5141	6142	4.7
C(13)	6717 (23)	3047 (29)	3612 (23)	5.4	H(143)	9181	6779	5339	4.7
C(140)	8146 (25)	4653 (28)	3776 (22)	5.7	H(144)	8518	6577	4587	4.7
C(141)	8316 (26)	4432 (29)	4753 (35)	7.4	H(145)	7587	5969	3595	4.7
C(142)	8731 (26)	5230 (27)	5399 (21)	5.0	H(141)′	10396	2970	3986	4.7
C(143)	8905 (28)	6138 (37)	4988 (55)	11.4	H(142)′	11486	4226	4246	4.7
C(144)	8666 (47)	6180 (45)	3741 (49)	12.7	H(143)′	10656	6421	3779	4.7
C(145)	8268 (28)	5445 (29)	3352 (27)	4.6	H(144)′	8715	6806	2515	4.7
C(22)	13213 (12)	1695 (13)	3697 (12)	6.1	H(145)′	8664	5560	2406	4.7
C(23)	12946 (13)	406 (20)	5561 (11)	7.7	H(241)	14630	−640	3068	4.7
C(240)	14020 (10)	−1070 (12)	4243 (9)	4.2	H(242)	15980	−2688	3189	4.7
C(241)	14685 (12)	−1319 (14)	3574 (12)	5.3	H(243)	16126	−4263	4404	4.7
C(242)	15482 (13)	−2486 (18)	3670 (18)	7.8	H(244)	14924	−3790	5498	4.7
C(243)	15530 (15)	−3338 (17)	4338 (18)	7.9	H(245)	13574	−1743	5376	4.7
C(244)	14862 (14)	−3087 (15)	4946 (13)	6.6	H(341)	9807	−2910	1077	4.7
C(245)	14124 (11)	−1969 (14)	4849 (11)	5.2	H(342)	8527	−3919	602	4.7
C(32)	13048 (23)	−4274 (30)	3051 (19)	6.7	H(343)	9094	−6112	1005	4.7
C(33)	12458 (16)	−3436 (16)	886 (19)	3.1	H(344)	10941	−7296	1884	4.7
C(340)	11104 (17)	−4513 (19)	1730 (15)	3.0	H(345)	11694	−5635	2730	4.7
C(341)	10098 (26)	−3901 (24)	1249 (23)	5.6	H(341)′	11716	−3352	−64	4.7
C(342)	9406 (31)	−4526 (30)	954 (24)	6.3	H(342)′	11185	−4640	−1291	4.7
C(343)	9706 (21)	−5726 (21)	1217 (18)	3.3	H(343)′	10957	−6476	−757	4.7
C(344)	10560 (37)	−6277 (29)	1714 (34)	7.5	H(344)′	11262	−7024	1004	4.7
C(345)	11434 (31)	−5733 (24)	1930 (20)	4.3	H(345)′	12138	−5824	951	4.7
C(42)	7005 (11)	−740 (19)	−399 (10)	6.8	H(441)	6224	409	2511	4.7
C(43)	6861 (10)	−1583 (12)	1589 (12)	5.4	H(442)	4869	2242	2865	4.7
C(440)	6035 (7)	1105 (10)	1052 (8)	2.9	H(443)	3920	3965	1606	4.7
C(441)	5834 (12)	1169 (14)	1964 (9)	5.6	H(444)	4326	3856	−9	4.7
C(442)	5059 (15)	2235 (18)	2153 (13)	7.5	H(445)	5682	2023	−363	4.7

[a] The prime designates conformer 2.

solution. These observations suggest that the compounds are dissociated in benzene through the loss of apical water molecule(s). In order to investigate the solution chemistry of these complexes, molecular weight, magnetic susceptibility, and ^1H NMR studies were carried out on solutions of some of the aquo complexes; cf. Tables IV–VI.

Molecular weight measurements by vapor-phase osmometry on THF solutions of the complexes $Cu(O_2CSiPhMe_2)_2 \cdot H_2O$ and $Cu(O_2CSiPh_2Me)_2 \cdot H_2O$ indicate that the dimer structure including the aquo ligands is largely maintained in solution. In benzene solution, where the color changes occur, molecular weight measurements on the complexes $Cu(O_2CMR_3)_2 \cdot H_2O$ (M = C, Si, Ge; R = Ph, Me) indicate that dissociation does occur and is a function of both M and R; cf. Table V. The predominant factor appears to be related to the number of phenyl groups attached to M: dissociation increases with the number of phenyl groups in the complex. Steric effects could account for the observed order.[24,25]

Magnetic studies on the aquo complexes in benzene-d_6 solution by the Evans method indicate that the dimeric structure is largely maintained; cf. Table IV. Since magnetic susceptibilities are not extremely sensitive to the nature of the apical ligand, these results are not surprising and are consistent with the previous studies on copper(II) carboxylates.[26-28]

The above results indicate that in benzene solution the dimeric complexes $[Cu(O_2CMR_3)_2 \cdot H_2O]_2$ (M = C, Si, Ge; R = Ph, Me) undergo dissociation through the loss of the aquo ligand(s), which results in the color changes, while maintaining the bridged binuclear structure.

The ^1H NMR data in acetone-d_6 for two copper(II) complexes, $Cu(O_2CSiPhMe_2)_2 \cdot H_2O$ and $Cu(O_2CSiPh_2Me)_2 \cdot H_2O$, are reported in Table VI, along with data on the zinc complex $Zn(O_2CSiPhMe_2)_2 \cdot 0.5H_2O$ and the conjugate acid form of the ligand, $PhMe_2SiCO_2H$, for comparison purposes. If considerable amounts of monomeric copper(II) species were present, large shifts in the resonance frequencies and severe line broadening would be expected due to the contact hyperfine interaction (Knight shift).[29]

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Table III. Important Bond Distances (Å) and Angles (deg) in $Cu_2(O_2CSiPhMe_2)_4{\cdot}2H_2O$

Distances			
Cu(1)–Cu(2)	2.578 (1)	C(11)–O(11)	1.557 (13)
Cu(1)–O(1)	2.301 (6)	C(11)–O(12)	1.203 (15)
Cu(1)–O(11)	1.832 (7)	C(21)–O(21)	1.155 (14)
Cu(1)–O(21)	2.010 (6)	C(21)–O(22)	1.387 (12)
Cu(1)–O(31)	2.103 (2)	C(31)–O(31)	1.285 (1)
Cu(1)–O(41)	1.893 (2)	C(31)–O(32)	1.159 (1)
Cu(2)–O(2)	2.080 (1)	C(41)–O(41)	1.187 (8)
Cu(2)–O(12)	1.868 (7)	C(41)–O(42)	1.366 (7)
Cu(2)–O(22)	2.070 (7)	Si(1)–C(11)	1.927 (14)
Cu(2)–O(32)	2.104 (1)	Si(2)–C(21)	2.005 (12)
Cu(2)–O(42)	1.924 (1)	Si(3)–C(31)	1.842 (8)
		Si(4)–C(41)	1.910 (10)
Angles			
Cu(1)–Cu(2)–O(2)	173.6 (2)	O(21)–Cu(1)–O(31)	92.9 (2)
Cu(2)–Cu(1)–O(1)	172.6 (1)	O(21)–Cu(1)–O(41)	173.4 (2)
Cu(1)–Cu(2)–O(12)	85.1 (1)	O(31)–Cu(1)–O(41)	87.5 (3)
Cu(1)–Cu(2)–O(22)	84.8 (1)	O(2)–Cu(2)–O(12)	98.0 (2)
Cu(1)–Cu(2)–O(32)	83.9 (2)	O(2)–Cu(2)–O(22)	89.5 (2)
Cu(1)–Cu(2)–O(42)	83.2 (2)	O(2)–Cu(2)–O(32)	92.5 (3)
Cu(2)–Cu(1)–O(11)	85.9 (1)	O(2)–Cu(2)–O(42)	102.8 (3)
Cu(2)–Cu(1)–O(21)	85.4 (1)	O(12)–Cu(2)–O(22)	91.1 (1)
Cu(2)–Cu(1)–O(31)	85.2 (2)	O(12)–Cu(2)–O(32)	168.1 (2)
Cu(2)–Cu(1)–O(41)	88.0 (2)	O(12)–Cu(2)–O(42)	82.4 (2)
Cu(1)–O(11)–C(11)	122.9 (5)	O(22)–Cu(2)–O(32)	83.4 (2)
Cu(1)–O(21)–C(21)	125.8 (5)	O(22)–Cu(2)–O(42)	166.8 (2)
Cu(1)–O(31)–C(31)	117.3 (4)	O(32)–Cu(2)–O(42)	100.8 (3)
Cu(1)–O(41)–C(41)	120.2 (4)	O(11)–C(11)–O(12)	112.3 (10)
Cu(2)–O(12)–C(11)	132.4 (6)	O(21)–C(21)–O(22)	122.6 (9)
Cu(2)–O(22)–C(21)	117.8 (5)	O(31)–C(31)–O(32)	129.9 (4)
Cu(2)–O(32)–C(31)	121.0 (4)	O(41)–C(41)–O(42)	127.0 (5)
Cu(2)–O(42)–C(41)	119.8 (5)	O(11)–C(11)–Si(1)	116.4 (8)
O(1)–Cu(1)–O(11)	97.2 (3)	O(21)–C(21)–Si(2)	126.3 (6)
O(1)–Cu(1)–O(21)	88.0 (2)	O(31)–C(31)–Si(3)	113.3 (3)
O(1)–Cu(1)–O(31)	91.6 (2)	O(41)–C(41)–Si(4)	122.1 (3)
O(1)–Cu(1)–O(41)	98.5 (2)	O(12)–C(11)–Si(1)	131.2 (9)
O(11)–Cu(1)–O(21)	85.1 (3)	O(22)–C(21)–Si(2)	109.5 (7)
O(11)–Cu(1)–O(31)	171.0 (2)	O(32)–C(31)–Si(3)	116.6 (3)
O(11)–Cu(1)–O(41)	93.5 (2)	O(42)–C(41)–Si(4)	107.5 (3)

Table IV. Magnetic Properties of $Cu(O_2CR)_2{\cdot}nL$

R	nL	$\chi_M \times 10^6$,[a] cgsu	$\chi'_M \times 10^6$, cgsu (T, K)[b,c]	μ_{eff},[d] μ_B
CMe_2Ph	H_2O	482[e]	698 (300)	1.24
$SiMe_2Ph$	H_2O	−68[e]	177 (302)	0.53
			142 (308)[f]	0.45
$CMePh_2$	H_2O	455[c]	746 (298)	1.28
			811 (308)[f]	1.37
$SiMePh_2$	H_2O	−95.7[g]	236 (297)	0.64
		−100[e]	232 (297)	0.64
			211 (308)[f]	0.61
CPh_3	$2H_2O$	543[g]	921 (296)	1.43
		562[e]	941 (298)	1.46
			903 (308)[f]	1.45
$SiPh_3$	H_2O	−93[g]	300 (296)	0.75
			370 (308)[f]	0.87
$GePh_3$	H_2O	−152[g]	254 (296)	0.68
			258 (308)[f]	0.70
$GePh_3$	py	−186[g]	269 (298)	0.71
$GePh_3$	Me_2SO	−188[g]	260 (298)	0.70
$GePh_3$	$2C_6H_5NH_2$	−307[g]	226 (298)	0.63

[a] Uncorrected. [b] Corrected for constituent atom diamagnetism by using Pascal's constants. [c] The $|-2J|$ values range from 585 to 897 cm^{-1} for the Si and Ge complexes and from 269 to 378 cm^{-1} for the C complexes when calculated from χ'_M by using the HVVD equation assuming $\bar{g} = 2.16$ and $N\alpha = 60 \times 10^{-6}$ cgsu. [d] Corrected for temperature-independent paramagnetism of Cu(II); cf. Experimental Section. [e] Gouy method. [f] Evans method. [g] Faraday method.

Only small paramagnetic shifts with some line broadening are observed, indicating that the copper(II) complexes are largely dimeric in acetone-d_6.

Table V. Molecular Weight Data for $Cu(O_2CR)_2{\cdot}H_2O$ in Solution at 37 °C

R	solvent	concn, M × 10^2	mol wt	% dissocn[a]
CMe_2Ph	benzene	0.760	763	7
$SiMe_2Ph$	benzene	0.545	809	9
	THF	3.03	848	8
$CMePh_2$	benzene	0.118	905	17
$SiMePh_2$	benzene	0.416	907	24
	THF	5.57	1075	5
$SiPh_3$	benzene	0.629	1070[b]	29
	benzene	0.532	1063[c]	29
$GePh_3$	benzene	0.653	1130	38

[a] Calculated by assuming one water molecule dissociates per dimer unit. [b] Mechrolab vapor-phase osmometer. [c] Knauer vapor-phase osmometer.

Table VI. Proton Magnetic Resonance Data[a]

compd	δ CH$_3$	δ Ph[b]	peak area ratio[c]
$Cu(O_2CSiMe_2Ph)_2{\cdot}H_2O$	0.18	7.27	1:0.83
$Cu(O_2CSiMePh_2)_2{\cdot}H_2O$	0.37	7.20	1:3.33
$Zn(O_2CSiMePh_2)_2{\cdot}0.5H_2O$	0.84	7.57	1:3.32
$MePh_2SiCO_2H$	0.83	7.58	1:3.33

[a] Spectra determined on a Varian Model EM-360, 60-MHz spectrometer in acetone-d_6 solution, concentration ca. 0.1–0.04 M, using Me_4Si as an internal standard. [b] Frequency of resonance taken as the center of the multiplet. [c] $CH_3{:}C_6H_5$.

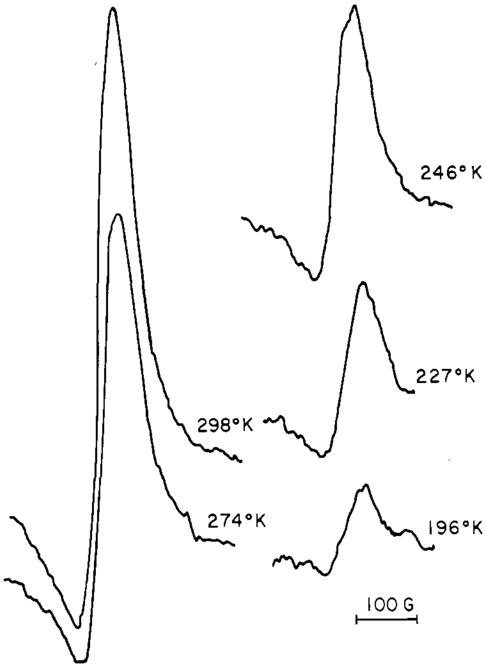

Figure 3. Variation of the ESR signal intensity, $H_\perp$, as a function of temperature for a powdered sample of $[Cu(O_2CSiPhMe_2)_2{\cdot}H_2O]_2$.

Electron Spin Resonance. The X-band ESR spectra of powdered samples of $[Cu(O_2CCR_3)_2{\cdot}nL]_2$ that have a copper(II) acetate monohydrate type structure have been extensively studied.[6,30,31] For the complexes with axial symmetry, the spectra show three absorptions that are characteristic of the triplet state ($D > h\nu$), designated H_{z_1}, $H_\perp$, and H_{z_2} in the order of increasing field strength, and one absorption characteristic of small quantities of a monomeric impurity (usually <2%).

The ESR spectra of the dimeric complexes $[Cu(O_2CMR_3)_2{\cdot}nL]_2$ (M = Si, Ge; R = Me, Ph; nL = H_2O, Me_2SO, py, $2C_6H_5NH_2$) are quite similar, showing a monomer absorption, ca. 3200 G, and a triplet absorption, ca. 5180 G (ca. 9.09 GHz). The $H_\parallel$ absorptions were not detected,[32] most probably due to their low

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(32) The ESR spectrum of one complex, $Cu(O_2CSiPhMe_2)_2{\cdot}H_2O$, was scanned to 10 000 G (9.63 GHz).

Table VII. Cu–Cu Distances and Singlet–Triplet Splittings in $[Cu(O_2CR)_2{\cdot}nL]_2$

no.	R	*n*L	Cu–Cu, Å	$-2J$, cm^{-1}	ref	
					structure	magnetism
1	$PhMe_2Si$	H_2O	2.578	1000 ± 150		
2	Me	H_2O	2.616	284	34	35
3	Et	0.5 dioxane	2.563	386	36	37
4	*n*-Pr	*a*	2.565	322	38	39
5	Et	*a*	2.578	300	40	39
6	H	0.5 dioxane	2.58	555	41	42
7	Me	0.5 pyrazine	2.583	320	43	43
8	Me	quinoline	2.642	320	44	45
9	CF_3	quinoline	2.886	310	46	46
10	CCl_3	2-Cl-py	2.766	217	47	47
11	CBr_3	2-Cl-py	2.766	180	48	48

[a] The carboxylate oxygen of an adjacent molecule is the ligand.

intensity[6,30,31] and the large zero-field splitting (vide infra). The absorption at ca. 5180 G is assigned as $H_\perp$ on the basis of its position, contour, and intensity.[31]

Variable-temperature ESR spectroscopy was employed to determine the singlet–triplet splittings, $-2J$, for the complexes $[Cu(O_2CSiR_3)_2{\cdot}H_2O]_2$, where R_3 = $PhMe_2$, Ph_2Me, and Ph_3, by the method of Wasson et al.[30] In these studies, the absorption assigned as $H_\perp$ was employed, the position being unchanged and the line width (70 G) remaining constant (<10% change) with the temperature variation (193–313 K) (see Figure 3). *The singlet–triplet splitting observed for the three complexes, $|-2J|$ = 1000 ± 150 cm^{-1}, is the largest reported for dimeric copper(II) carboxylates.*[33]

The zero-field splitting parameter, *D*, can be calculated for the complexes $[Cu(O_2CMR_3)_2{\cdot}nL]_2$ (M = Si, Ge) on the basis of the above assignment, if one assumes a typical value for $g_\perp$ ($g_\perp \approx 2.09$ for dimeric copper(II) carboxylates[19,31]). For example, $D = 0.52$ cm^{-1} is calculated for the complex $[Cu(O_2CSiPhMe_2)_2{\cdot}H_2O]_2$ ($H_\perp$ = 5118 G, 9.08 GHz). This is the largest zero-field splitting parameter reported for dimeric copper(II) carboxylates.

The above results readily explain the difficulties encountered in obtaining ESR spectra of the silicon and germanium complexes. With application of Boltzmann's distribution (25 °C), the triplet state of the silicon complexes has an occupancy of ca. 2–3%, whereas in copper(II) acetate monohydrate, the triplet state has an occupancy of 43%.

Discussion

The structure of $[Cu(O_2CSiMe_2Ph)_2{\cdot}H_2O]_2$, while exhibiting an unusual distortion of the cage, cannot be used to explain the much larger $|-2J|$ values observed for the copper(II) complexes of carboxysilanes and -germanes. The magnetic moments are the same within experimental error in both the solid state and benzene solution, and it is unlikely that the cage distortion is maintained in solution. The Cu–Cu distance in the above complex, while shorter than reported for the copper(II) acetate monohydrate dimer, is similar to the distances reported for a number of complexes that have singlet–triplet splittings in the range $|-2J|$ = 300–555 cm^{-1}; cf. Table VII, no. 1–7. These data emphasize that there is no direct relationship between the Cu–Cu distance and the $|-2J|$ value. Similarly, Doedens et al. have shown that a longer Cu–Cu distance does not necessarily mean a smaller $|-2J|$ value, Table VII, no. 8 and 9,[46] and that the relationship is complex, Table VII, no. 10 and 11.[47,48] Porter and Doedens have pointed out that there is an apparent relationship between the $|-2J|$ value and the polarizability of the carboxylate ligand.[48]

The above results will be discussed qualitatively in terms of the effect of the metalloid, silicon in particular, on the singlet–triplet separation in copper(II) acetate monohydrate type dimers in terms of the MO analysis of Hoffmann et al.[49] and de Loth et al.[50] (cf. the latter paper for a brief synopsis of previous studies on exchange interactions in these complexes).

The most recent and complete MO treatment of exchange interactions in copper(II) acetate monohydrate indicates that the contributions to the singlet–triplet energy splitting, $-2J$, are of four major types: direct exchange (ferromagnetic); superexchange, SE (antiferromagnetic); double-spin polarization, DSP (overall antiferromagnetic); higher order effects, SE, SE + P (antiferromagnetic).[50]

The unusually large $|-2J|$ values observed for copper(II) complexes of carboxysilanes can be explained in terms of a SE mechanism in which the electronic effect of silicon on the MO levels of the carboxylate ligand is considered. According to the model of Hoffmann et al.,[49] the singlet–triplet separation arises from the interaction between the $d_{x^2-y^2}$ orbitals of the $(Cu^{2+})_2$ system, d_S and d_A, and the HOMO of the carboxylate ligand, l_S and l_A. The l_S orbital is pushed to higher energy than the l_A orbital because of the antibonding interaction with the C–C bonding orbital. In the silanecarboxylate ion, CNDO/2 MO calculations indicate that the l_S orbital is higher in energy and the l_A orbital is lower in energy than observed for the carbon analogues,[51] which undoubtedly results from the $+I$ effect of silicon.[8,52] As a result of the energy matching between the ligand and metal orbitals, a larger splitting between the singlet and triplet states is expected when silicon is present in the carboxylate ligand.

The substitution of silicon for carbon in the α-position of the carboxylate ligand results in a lowering of the energy of the π system of the carboxylate group, particularly the π^* level

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(33) The singlet–triplet separation in $Cu(O_2CMPh_3)_2{\cdot}Me_2SO$ (M = Si, Ge), $-2J \approx 1200$ cm^{-1}, recently has been determined from variable-temperature magnetic susceptibility measurements (Faraday method): Kato, M.; Taura, T.; Steward, O. W.; Tokii, T.; Muto, Y.; Kushi, Y.; Suzuki, I. Proceedings, 33rd Conference on Coordination Chemistry of the Chemical Society of Japan, Toyonaka, Oct 1983; p 494.

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(52) A stronger ligand field results when Si or Ge is substituted for C in the α-position of the carboxylate ion; band I (visible region) is shifted to higher energy; cf. ref 2. A subsequent paper will deal with the electronic spectral properties of these compounds.

Inorg. Chem. **1986**, *25*, 777–788 777

(CNDO/2 calculations).[51] This effect will enhance the singlet-triplet separation since exchange through the π system by the DSP mechanism is inversely related to the energy difference between the π and π^* levels. Gerloch and Harding[53] also have reported semiempirical MO calculations in support of a π-type mechanism for superexchange.

de Loth et al.[50] have reported that higher order effects, SE, SE + P, contribute to the singlet–triplet splitting. The presence of an α-silicon atom in the ligand should enhance this effect by increasing the polarizability of the ligand. Kuznesof et al. have suggested that the greater stability of $H_3SiCO_2^-$, as compared to $H_3CCO_2^-$, is related to the greater polarizability of silicon.[51]

In conclusion, the large singlet–triplet splittings observed for copper(II) complexes of carboxysilanes and -germanes undoubtedly arise from the ability of the metalloid to interact with both the σ and π systems of the carboxylate group and to enhance the polarizability of the ligand.

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Registry No. $[Cu(O_2CCMe_2Ph) \cdot H_2O]_2$, 100229-28-5; $[Cu(O_2CSiMe_2Ph) \cdot H_2O]_2$, 100229-29-6; $[Cu(O_2CMePh_2) \cdot H_2O]_2$, 100229-30-9; $[Cu(O_2CSiMePh_2) \cdot H_2O]_2$, 100229-31-0; $[Cu(O_2CCPh_3) \cdot H_2O]_2$, 100229-32-1; $[Cu(O_2CSiPh_3) \cdot H_2O]_2$, 100243-55-8; $[Cu(O_2CGePh_3) \cdot H_2O]_2$, 100243-56-9; $[Cu(O_2CGePh_3) \cdot H_2O]_2$, 100243-57-0; $[Cu(O_2CGePh_3) \cdot H_2O]_2$, 100243-58-1; $[Cu(O_2CGePh_3) \cdot H_2O]_2$, 100243-59-2; $[Zn(O_2CSiMePh_2) \cdot 0.5H_2O]_2$, 100229-33-2.

Supplementary Material Available: Tables of analytical data, observed and calculated structure factors, thermal parameters, bond distances and angles, and intermolecular distances between **1** and **2** and a stereoscopic view of the unit cell of **1** (24 pages). Ordering information is given on any current masthead page.

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Preparations, Raman Spectra, and Crystal Structures of $(SCl_3)(SbCl_6)$, $(SeCl_3)(SbCl_6)$, $(SBr_{1.2}Cl_{1.8})(SbCl_6)$, $(TeCl_3)(AlCl_4)$ (Triclinic Modification), $(TeCl_3)(SbF_6)$, $(TeCl_3)(AsF_6)$, and $(TeF_3)_2(SO_4)$

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The preparations, Raman spectra, and crystal structures of the compounds $(SCl_3)(SbCl_6)$ (**1**), $(SeCl_3)(SbCl_6)$ (**2**), $(SBr_{1.2}Cl_{1.8})(SbCl_6)$ (**3**), $(TeCl_3)(AlCl_4)$ (**4**), $(TeCl_3)(AsF_6)$ (**5**), $(TeCl_3)(SbF_6)$ (**6**), and $(TeF_3)_2SO_4$ (**7**) are reported. Crystal data are as follows: **1**, monoclinic, space group $C2/m$, $a = 12.385$ (2) Å, $b = 7.774$ (1) Å, $c = 13.959$ (3) Å, $\beta = 108.06$ (1)°, $V = 1277.8$ Å^3, and $D_c = 2.46$ g cm^{-3} for $Z = 4$; **2**, trigonal, space group $R\bar{3}m$, $a = 8.840$ (5) Å, $\alpha = 74.89$ (5)°, $V = 630.0$ Å^3, and $D_c = 2.74$ g cm^{-3} for $Z = 2$; **3**, trigonal, space group $R\bar{3}m$, $a = 8.871$ (2) Å, $\alpha = 74.11$ (2)°, $V = 630.7$ Å^3, and $D_c = 2.77$ g cm^{-3} for $Z = 2$; **4**, triclinic, space group $P\bar{1}$, $a = 6.554$ (1) Å, $b = 16.691$ (4) Å, $c = 8.391$ (1) Å, $\alpha = 92.79$ (1)°, $\beta = 97.31$ (1)°, $\gamma = 96.11$ (1)°, $V = 1065.8$ Å^3, and $D_c = 2.51$ for $Z = 4$; **5**, monoclinic, space group $P2_1/n$, $a = 8.827$ (2) Å, $b = 10.009$ (3) Å, $c = 10.592$ (5) Å, $\beta = 108.27$ (3)°, $V = 888.7$ Å^3, and $D_c = 3.26$ g cm^{-3} for $Z = 4$; **6**, orthorhombic, space group $Pnma$, $a = 17.031$ (3) Å, $b = 8.460$ (1) Å, $c = 6.398$ (1) Å, $V = 921.8$ Å^3, and $D_c = 3.38$ g cm^{-3} for $Z = 4$; **7**, orthorhombic, space group $P2_12_12_1$, $a = 8.758$ (1) Å, $b = 8.983$ (1) Å, $c = 9.946$ (2) Å, $V = 8.983$ Å^3, and $D_c = 3.95$ g cm^{-3} for $Z = 4$. Crystals of $(TeCl_3)(SbCl_6)$ and $(TeCl_3)(NbCl_6)$ are isomorphous, monoclinic, space group $C2/c$, with cell dimensions ($NbCl_6^-$ salt in brackets) $a = 22.137$ (4) Å [21.858 (4) Å], $b = 12.781$ (2) Å [12.622 (3) Å], $c = 19.308$ (3) Å [19.048 (3) Å], $\beta = 112.47$ (1)° [112.48 (1)°], $V = 5048$ (2) Å^3 [4856 (3) Å^3], and $D_c = 2.99$ g cm^{-3} [2.95 g cm^{-3}] for $Z = 16$. All the MX_3^+ cations in these compounds are involved in significant anion–cation secondary bonding interactions of varying strengths and geometries. Trans relationships between the lengths of these interactions and primary bond lengths and their effects on the primary bonding geometries of the cations are discussed and compared to those of related compounds. The $SBr_{1.2}Cl_{1.8}^+$ cation in the hexachloroantimonate salt consists of a disordered mixture of $SBr_xCl_{3-x}^+$ cations. The tetrachloroaluminate salt of $TeCl_3^+$ is a different modification with a crystal packing significantly different from that previously reported.

Introduction

An important feature of the crystal structures of salts containing MX_3^+ cations (M = S, Se, Te; X = F, Cl, Br, I) is the strong secondary interactions[1] between the cations and the accompanying anions. These interactions generally form around the lone pair of electrons on the central atom M in directions that are approximately capping faces (Y contacts) or bridging edges (Y′ contacts) of the polyhedron describing the primary geometry.[2] With the exception of $(TeF_3)(Sb_2F_{11})$, all reported structures containing MX_3^+ cations have three face-capping M···Y secondary interactions approximately trans to the primary bonds to give distorted monocapped octahedra AX_3Y_3E about M with the lone pair as the cap. In this paper we report the Raman spectra and crystal structures for the compounds $(SCl_3)(SbCl_6)$, $(SeCl_3)(SbCl_6)$, $(SCl_{1.2}Br_{1.8})(SbCl_6)$, $(TeCl_3)(AlCl_4)$, $(TeCl_3)(SbF_6)$, $(TeCl_3)(AsF_6)$, and $(TeF_3)_2(SO_4)$ and discuss trends in the overall MX_3^+ geometry and the strength of the anion–cation interactions with changing M and/or X in these and related salts. The tetrachloroaluminate salt of $TeCl_3^+$ is a different modification (triclinic) from that previously reported (monoclinic).[3]

Experimental Section

Materials. Sulfur (BDH, sublimed), selenium (Alfa Inorganics), and tellurium (Alfa Inorganics) were dried under vacuum at 20 °C. Arsenic (Alfa Inorganics) was heated under vacuum at 200 °C to sublime off the oxide. Bromine (Fisher Scientific Co.), methylene chloride (Fisher

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