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Tetranuclear Complexes of Trigonal-bipyramidal Copper(II). III.[1] Eletcronic and Infrared Spectra

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Electronic spectral data of forty μ_4-Oxo-hexa-μ-halogeno copper complexes $Cu_4OX_6L_4$ (X = halide, L = neutral or anionic ligand) with the metal in trigonal-bipyramidal coordination are given. Two absorptions about 10 and 12 kK are assigned to the two ligand field transitions, the two other absorptions (for neutral complexes) are of charge transfer type ($X \rightarrow Cu$). The FIR data for several complexes are presented and some tentative assignments made.

Introduction

Pentacoordination is now a common feature in transition metal complex chemistry;[2] but most copper (II) complexes with this coordination number have been synthesized with chelating ligands.[3] No systematic variation of ligands in trigonal-bipyramidal copper complexes has been performed because of the preferred tetra- or hexacoordination. Since 1966 complexes of general composition $Cu_4OX_6L_4$ (X = Halide, L = neutral or anionic ligand) have been reported independently by several groups.[4-6] Their structures have unambiguously been determined by several single crystal x-ray studies and contain a central oxo anion, tetrahedrally coordinate by four copper(II) ions, these being bridged in pairs by six halide ions.[7-11]

We recently published simple and yielding syntheses for numerous hexachloro and -bromo complexes, where one axial ligand is easily varied.[1] We now report infrared and electronic spectral data for these compounds.

Experimental Section

Preparation. Anhydrous copper(II) chloride or bromide and copper(II) oxide are refluxed with the exclusion of moisture in donor solvents like methanol, acetone or acetonitrile. From concentrated alcoholic solutions complexes of analytical composition $Cu_4O(Hal)_6(CH_3OH)_6$ crystallize, which loose more than two moles of methanol when heated to 60-80° in vacuo. To accelerate the reaction an excess of cupric oxide (the theoretical ratio $CuO:CuX_2$ is 1:3) is recommended, which is filtered off after 2-4 hrs. refluxing. For the preparation of complexes $Cu_4OX_6L_4$ with L other than the solvent, the filtered solution is diluted with ether or ether/acetone and he ligand slowly added as diluted solution, too, to avoid precipitation.

Careful work gives analytically pure and crystalline material of dark yellow to black colour depending on crystal size and axial ligand L. All complexes not described previously[1] have been prepared by this improved method, in general with acetone as solvent.

Most compounds are hydrolysed in moist air, some are rather sensitive to heat.

Spectra. Electronic spectra where recorded with a CARY 14 in chloroform or as polycrystalline material in Nujol mull. Very good spectra where obtained, as chequed with the corresponding solution spectra, when a sample, finely dispersed in Nujol, was brought on a filter paper, with a Nujol-treated paper on the reference side, too.[12] Good results were also obtained with grinding the samples on an etched quartz plate. Both plates or papers were placed at the entrance of the detector housing.

Infrared spectra where throughout recorded as Nujol/PFE mulls. KBr pellets were discarded because of the simple exchange reaction bromide ion vs. axial ligand.

IR-spectra were recorded with a Perkin-Elmer 325 spectrometer, far infrared data were taken with a Beckman IR-11.

Electronic Spectral Data. The solubilities of the tetranuclear complex are quite different, depending on the axial ligand L and only to a small extend on the bridging halogen X. The best solvent for quantitative absorption measurements in the visible and near ultraviolet region was chloroform. The solubi-

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lity of the neutral complexes was sufficient, ligand exchange reaction were not observed, osmometric measurements showed no dissociation. Several complexes were recrystallized from the solvent to prove its inertness.

Table I gives absorption maxima and molar extinc-

Table I. Solution spectra of tetranuclear complexes $Cu_4OX_6(Ligand)_4$ (ν_m in cm^{-1}; ε_m in 1000 cm^2/mole).

Nr.	Ligand	ν_1 (ε_1)	ν_2 (ε_2)	ν_3[b] (ε_3)	ν_4 (ε_4)
	$Cu_4OCl_6(Ligand)_4$				
I	pyridine	11300 (1120)	13330[a] (1030)	28170 (3380)	38460 (19600)
II	2-methyl-pyridine	10870[b] (440)	13610 (720)	27780 (4640)	38460[c] (18400)
III	2-chloro-pyridine	10420 (700)	12820 (720)	27780 (3220)	37040[d] (18300)
IV	3-methyl-pyridine	11170 (1060)	13250[a] (980)	27780 (4840)	37740 (53000)
V	4-methyl-pyridine	11300 (1100)	13250[a] (1020)	28170 (4800)	38460 (62000)
VI	quinoline	10990 (550)	13330 (750)	27400 (1500)	33900[e] (27400)
VII	diisopropylcarbodiimide	10580 (820)	12660 (720)	27780 (3000)	37040 (12800)
VIII	N-cyano-pyrrolidine	10530 (810)	12580 (740)	27780 (2660)	36360 (15500)
IX	acetonitrile	10580 (750)	12580 (690)	28170 (2100)	37040 (15200)
X	phenylacetonitrile	10360 (840)	12500 (800)	28170 (2400)	37040 (15700)
XI	benzonitrile	10470 (770)	12500 (720)	27400 (3000)	31950 (7500)
XII	tetramethylurea	10360 (870)	12420 (860)	28170 (2650)	36360 (15500)
XIII	N.N-dimethylacetamide	10360 (890)	12500 (840)	27780 (2610)	35710 (41500)
XIV	dimethylsulfoxide	10420 (630)	12820 (600)	—	36360 (10000)
XV	acetone	10360 (680)	12660 (620)	28990 (2800)	37740 (19500)
XVI	methanol	10530 (640)	12500 (590)	28170 (1680)	37040 (11200)
XVII	triphenylphosphinoxide	10200 (600)	12500 (600)	—	—[f]
	$Cu_4OBr_6(Ligand)_4$				
XVIII	pyridine	11100 (1760)	13160[a] (1670)	21280 (2100)	32260 (20200)
XIX	2-methyl-pyridine	10640[b] (530)	13420 (1080)	24390 (5040)	31750 (15600)
XX	2-chloro-pyridine	10310 (1430)	12270 (1350)	22730 (3120)	32260 (15700)
XXI	3-methyl-pyridine	11110 (1730)	13160[a] (1660)	21280 (1220)	32790 (15000)
XXII	4-methyl-pyridine	11110 (1760)	13160[a] (1700)	21740 (2160)	32260 (20300)
XXIII	quinoline	10750 (660)	13330 (1070)	23810 (3500)	32260[e] (27000)
XXIV	quinoxaline	10100 (750)	12350 (1170)	22730 (1960)	32260 (28000)
XXV	diisopropylcarbodiimide	10310 (1450)	12420 (1350)	22730 (1590)	32260 (16600)
XXVI	N-cyano-pyrrolidine	10310 (1560)	12270 (1470)	22220 (1830)	32260 (19800)
XXVII	acetonitrile	10260 (1480)	12200 (1420)	22730 (1750)	32260 (17900)
XXVIII	tetramethylurea	10260 (1420)	12270 (1340)	23810 (2300)	32260 (16700)
XXIX	N,N-dimethylacetamide	10260 (1550)	12200 (1490)	22200 (1550)	32260 (17300)
XXX	dimethylsulfoxide	10310 (1600)	12200 (1540)	22200 (1580)	32260 (18200)
XXXI	methanol	10310 (1470)	12120 (1440)	22200 (1440)	32260 (16600)

[a] further shoulder at 23000 (X = Cl) or 18000 (X = Br), due to impurities of trivial complex with coordination number four. [b] shoulder; [c] further peak at 34480 (13600); [d] another shoulder at 35090 (17000); [e] sharp absorption band at 31750 (26000) of quinoline itself; [f] in acetone because of solubility.

Table II. Solid spectra of tetranuclear complexes $Cu_4OX_6L_4$ (in cm^{-1}).

	Ligand	ν_1	ν_2	ν_3[a]	ν_4
	$Cu_4OCl_6L_4$				
I	pyridine	11360	13160	27780	34480
II	2-methyl-pyridine	11490	12990	28170	38460[d]
XIV	dimethylsufoxide	10310	12660	29410	37040
XVII	triphenylphosphinoxide	10420	12200	27780	37040
XXXII	pyridine-N-oxide	10640	12660	30300	38460
XXXIII	chloride (potassium)	9800	11900	29410[c]	37040
XXXIV	chloride (ammonium)	9520	11630	29410[c]	37040
XXXVII	chloride (TMA)[d]	9620	11760	29410[c]	37040
XVIII	bromide (TMA)	9710	11490	27030[c]	35710
XXXVIII	cyanide (TMA)	9520	11900	30300[c]	36360
	$Cu_4OBr_6L_4$				
XXXV	pyridine	11240	12500	21280	31750
XXXIX	chloride (TMA)	10100	11490	20830	33330
XXXVI	bromide (TMA)	10300	11900	22950	30300

[a] ν_3 is, in general, only visible as a shoulder; [b] band at 34480; [c] in the salts another shoulder appears between ν_2 and ν_3; [d] TMA = Tetramethylammonium cation.

tion coefficients for the first four maxima or shoulders. The two long wavelength absorptions overlap to an extend that ν_m and ε_m values cannot be taken "By inspection". For all spectra the values ν_1, ε_1, ν_2, and ε_2 have been obtained by graphic Gaussian analysis. As the bands at higher energies are unimportant for the interpretation of the ligand field characteristics (and as the spectra are not very well resolved in the charge-ransfer part) we renounced to make such an analysis in this part too. ε_m values are those taken from the recorded spectrum.

The salt-like complexes with anionic ligands L are unsoluble in chloroform. Solid spectra with a modified "grease-spot" method[12] were as well resolved as the solution spectra. This is another indication that no dissociation or exchange occurs in solution. Solid state spectra could not be taken in KBr pellets because the large excess of bromide ion leads to a substitution of some labile axial ligands.[13]

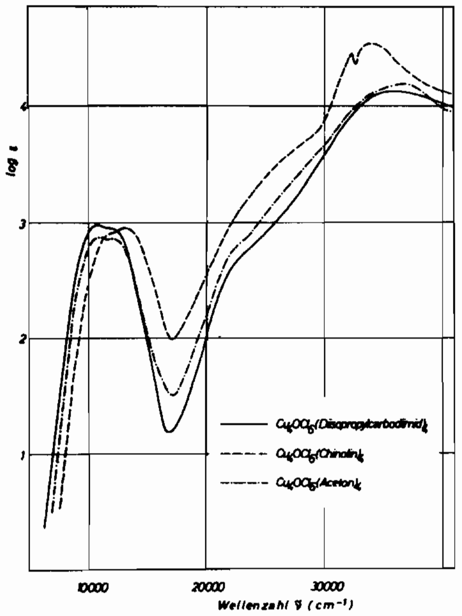

Figure 1. Electronic Spectra of complexes VI, VII and XV in chloroform solution.

Table II gives values for solid state spectra of anionic complexes and neutral complexes (for comparison with solution-spectra of Table I).

Figures 1 and 2 give some representative solution spectra of chloro- and bromo complexes, while Figure 3 shows the solid spectra of two anionic complexes in comparison to the solid spectrum of the pyridine complex I.

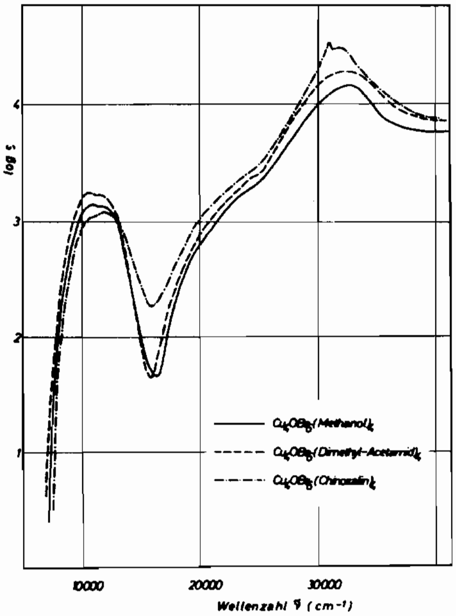

Figure 2. Electronic spectra of bromo complexes XXIV, XXIX and XXXI in chloroform solution.

The first double band ν_1, ν_2 is influenced more by the nature of the axial ligand than by the bridging halide, while ν_3 and ν_4 characteristically depend on this latter.

If one defines the total width of the ν_1,ν_2-double band as the difference between most separated points

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(13) A long wavelength shift of v_1 and v_2 was observed for XVII when the solid spectrum was taken in a KBr pellet.[8] This is not observed with our method. here no ligand exchange can occur.

Table III. Orbital representation in C_{3v} (D_{3h}).

C_{3v}	D_{3h}	metal orbitals	ligand orbitals * a = axial, e = equatorial
A_1	A_1'	4s	$\sigma^1+\sigma^2+\sigma^3$
		$3d_{z^2}$	$\sigma^O+\sigma^L$
	A_2''	$4p_z$	$\sigma^O-\sigma^L$
			$p_a^1+p_a^2+p_a^3$
A_2	A_2'		$p_e^1+p_e^2+p_e^3$
E	E′	$3d_{x^2-y^2}$	$2p_e^1-p_e^2-p_e^3$; $p_e^2-p_e^3$
		$4p_x$; $4p_y$	$2\sigma^1-\sigma^2-\sigma^3$; $\sigma^2-\sigma^3$
	E″	$3d_{xz}$; $3d_{yz}$	$2p_a^1-p_a^2-p_a^3$; $p_a^2-p_a^3$
			$2p^L$

* normalizing factors omitted; 1, 2, 3 are the three equatorial halide ligands, O (oxygen) and L (ligand) are the axial ones.

Table IV. Absorptions (and extinction coefficients) ν_1 and ν_2 for trigonal-bipyramidal copper(II) complexes.

Compound	ligand (equat.)	ligand (axial)	ν_1 (1)	ν_2 (2)	Lit.
$[Cu(NH_3)_2(NCS)_3]^-$	N	N	12800	14500	17
$[Cu(Tri\text{-}S\text{-}N)Br]^+$	S	N / Br	11800	14800	19
			(390)	(240)	
$[Cu(Me_6tren)NO_3]^+$	N	N / O	11200	14300	19
$[Cu(Me_6tren)ClO_4]^+$	N	N / O	11200	13800	19
$Cu_4OCl_6(py)_4$	Cl	N / O	11300	13300	
			(280)	(260)	
$Cu_4OBr_6(py)_4$	Br	N / O	11100	13160	
			(440)	(420)	
$[Cu(Me_6tren)Br]^+$	N	N / Br	10400	13300	19
			(450)	(210)	
$[Cu_4OBr_{10}]^{4-}$	Br	O / Br	10300	11900	
$[Cu_4OCl_{10}]^{4-}$	Cl	O / Cl	9600	11800	
$[CuCl_5]^{3-}$	Cl	Cl	8300	10400	14,18
			9000	11000	

of the individual bands, where $\varepsilon = 1/2\ \varepsilon_{max}$, typical values of 4000-4500 cm^{-1} are obtained. Bulky ligands like the 2-substituted pyridines or quinoline show total widths of 5000-5800 cm^{-1}. This is an indication of steric interferences, which might lift the degeneracy of electronic levels, as will be discussed later.

In the third figure additional shoulders resp. maxima are clearly recognisable for the anionic species between ν_2 and ν_4.

Typical differences in the electronic spectra of complexes $Cu_4OX_6L_4$ with trigonal-bipyramidal coordina-

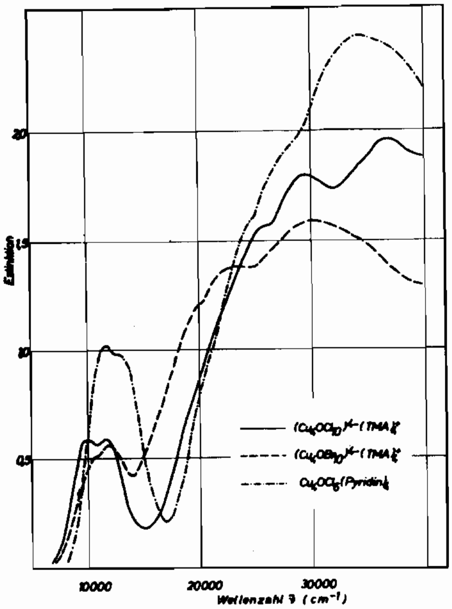

Figure 3. Solid spectra of complexes I, XXXV and XXXIX. (Extinction is to an arbitrary scale).

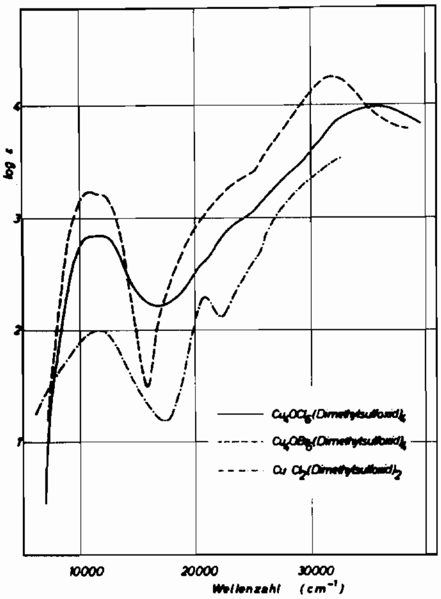

Figure 4. Comparison of electronic spectra of $Cu_4OX_6L_4$ and $CuCl_2L_2$ (L = dimethylsulfoxide) in chloroform solution.

tion and complexes CuX_2L_2 with (distorted) square planar coordination are demonstrated in Figure 4. There is one weaker band in the 11000/cm region with a shoulder on the long wavelength side and, characteristically, one extra sharp absorption at about 21-23000/cm for chloro complexes and about 17-18000/cm for bromo complexes, indicating charge-transfer type absorptions.

The ν_1, ν_2 double band seems to be very typical for pentacoordinated copper(II). Except for $[CuBr_5]^{-3}$, where the broad band about 8700/cm was not resolved,[14] all other trigonal-bipyramidal copper compounds show two absorptions (see Table IV).

Discussion

The tetranuclear complexes have been shown to contain four almost independent copper(II) ions. Barnes, Inman, and Hatfield[15] determined the coupling constant for the tetrahedral arrangement of copper ions with $J = -16$ cm^{-1} in XXXV. Other magnetic measurements show a slight increase of the magnetic moment when the temperature is lowered[16] and the most recent magnetic studies show a distinct difference between the anion XXXV and some neutral complexes (like XVII and XVIII),[16a] which might be understood in terms of degeneracy of the lowest orbital levels of the clusters.

The site symmetry at each of the copper ions is C_{3v}. The high svmmetry of the idealized $Cu_4OX_6L_4$ system (T_d) does not affect selection rules for C_{3v}. It is easily shown that any four tetrahedrally arranged vectors of C_{3v} (or vector pairs in E) will transform in T_d in a way that their representation contains at least one irreducible representation of type T being independent of Cartesian axes. Thus no transitions will occur within the cluster which prefer one direction or one copper ion. The idealized arrangement of atoms (or groups L) is shown in Figure 5.

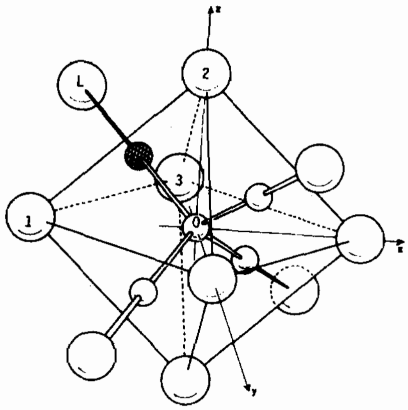

Figure 5. Idealized arrangement of atoms in the $Cu_4OX_6L_4$ system (copper-halogen bonds not shown).

To compare our spectral data with other C_{3v} and D_{3h} copper(II) complexes orbitals are listed as to their representation in these groups in the Table III.

Under the assumption of equal bond length and neglecting π-bonding the ^2D term of the cupric ion splits according to the scheme given.[17]

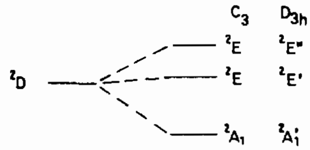

Figure 6. Splitting of the ^2D term in trigonal fields.

In C_{3v} two allowed ligand field transitions are to be expected, $^2E^{(1)} \leftarrow {}^2A_1$ and $^2E^{(2)} \leftarrow {}^2A_1$. It is interesting to compare this with the transitions in D_{3h}. The transition of lower energy $^2E' \leftarrow {}^2A_1'$ should be symmetry-allowed, while $^2E'' \leftarrow {}^2A_1'$ should be forbidden. This fact has led to considerable confusion in the interpretation of the ligand field spectra of cupric ions in trigonal fields. As shown in Table IV two long wavelength transitions (of almost equal intensity have been observed for the pentachlorocuprate[18] and other D_{3h} complexes[17] as well as for Ciampolini's complexes with tripod ligand.[3,19]

The accuracy of the data in Table IV should not be over-estimated. The two broad bands overlap strongly, so that appreciable differences occur when the maxima are determined either by inspection or by Gaussian analysis. Besides, in the case of $[CuCl_5]^{3-}$ a strong temperature dependence was observed.[18] Obviously the variation of the three equatorial ligands is less effective than the variation of the axial ligands; the same holds for the values of Table I.

In trigonal fields we expect two ligand field transition. Therefore the two bands ν_1 and ν_2 have been ascribed to these transitions.[18,20] On the other hand calculations on $[CuCl_5]^{3-}$ with the simple point charge model and more sophisticated treatments place the first ligand field transition at much lower energies.[21-23] But down to 5500 cm^{-1} we could not detect another absorption band, although the low energy transition should have comparable or greater intensity than the high energy one, as long as one accepts the splitting pattern of Figure 6. This pattern assumes five equidistant ligands.[23] Hatfield et al[22] in their modified Wolfsberg-Helmholz treatment of the pentachlorocuprate(II) ion started with Cu–Cl interatomic distances given by Mori.[24] Bernal et al[25,26] revised these data

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and showed the axial bonds with 2.296 Å to be much shorter than the equatorial bonds (2.391 Å). Obviously a one-parameter MO method as previously used by Day and Jørgensen[23] for this problem cannot take into account these short bonds. Bertrand and Kelley found an even shorter axial Cu–Cl bond in the $Cu_4OCl_{10}^{4-}$ ion (XXXV) (2.17 Å; 2.25 Å; two independent molecules in the unit cell).[9]

Recently Ludwig and Textor[27] described the electronic spectra of trigonal-planar halogenocuprates(II) $[CuX_3]^-$ in solution. These can be regarded as one extreme in the trigonal ligand fields, with the axial field equal to zero, the other extreme would be linear L–Cu–L, with no equatorial field. The shortened axial bonds in trigonal-bipyramidal complexes tell us that relativ orbital energies will be closer to the latter extreme than to the former. In Figure 7 a qualitative representation of orbital energies is given depending on the relative axial vs. equatorial field strength.

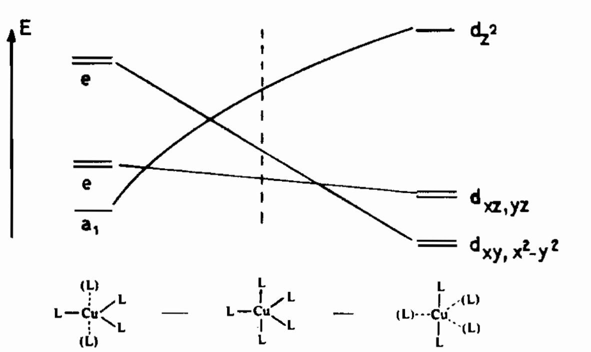

Figure 7. Dependence of orbital energies (schematically) on relative axial vs. equatorial field strength The dashed line gives the situation for five equidistant ligands).

While Ludwig and Textor have shown the situation on the left side of Figure 7 to occur, the situation in our complexes with shorter axial bonds is of course at the right side of the figure.

Here we approach the situation, where the two e-orbitals cross. But of course the corresponding E states will not have the same energy. The almost constant energy difference of the two bands ν_1 and ν_2 might be caused by configuration interaction. The almost equal intensities can also be rationalized in terms of this mixing.

The slightly enhanced redox stability of trigonal-bipyramidal complexes is a consequence of the $^2A_1$ ground state, which makes the d_{z^2} more antibonding than the $d_{x^2-y^2}$ in the other coordination geometries.

The absorptions ν_3 and ν_4 (and occasionally further bands) give also some indication for this. The three equatorial halogens have one p-type lone pair each ($p_{equatorial}$, p_e). The others are involved in σ-bonds, so from these long wavelength CT transitions are not to be expected. As shown in Table III the three p_e orbitals give the representations A_2+E. As there is no metal orbital of representation A_2, the A_2 halogen orbital is nonbonding with respect to the metal and antibonding with respect to a single halide lone pair (interligand destabilisation). On the other hand the E halogen orbital is stabilized by interaction with metal orbitals of like symmetry. Thus we expect two halogen-to-metal charge transfer transitions, $^2A_2 \leftarrow {}^2A_1$, which is symmetry-forbidden, and $^2E \leftarrow {}^2A_1$ which is of higher energy and symmetry allowed. The absorptions ν_3 and ν_4 are therefore assigned to these two transitions; ν_3 in practically all cases appears as a rather weak shoulder about 10000/cm to lower energies relative to ν_4, which is at 38000/cm for chloro complexes and at 32000/cm for the bromo series. The anionic complexes $[Cu_4OX_6Y_4]^{4-}$ (Y = halide) should show another CT transition stemming from the degenerate pair of p-orbitals at the axial halide.[18,28] This CT absorption is expected between ν_3 and ν_4 because this pair of p-orbitals does not suffer interligand destabilisation (p_e: a_2) nor stabilisation (p_e: e) like the equatorial halide lone pairs. This third CT transition occurs at 26350-27000 cm for the $[Cu_4OCl_{10}]^{4-}$ depending on the cation. For $[Cu_4OBr_{10}]^{4-}$ this shoulder is at 20400 cm. For $K_4Cu_4OCl_{10}$, XXXIII, the strong band at 37040 (ν_4) is split. The asymmetric Cu_4O stretching frequency in the infrared is split, too. The rather small cation potassium migth be responsible for a distortion of the anionic chromophore.

Infrared spectral data. In the complex $Cu_4OX_6L_4$ the infrared active vibrations assignable to the coordinated ligand L do not differ significantly from other transition metal complexes with these ligands.[29] One exception is of course Bertrand's triphenylphosphinoxide complex,[8] where the P=O frequency is raised. We are especially interested in the vibrations of the central Cu_4OX_5 part of T_d symmetry. The simplest molecule available is the $[Cu_4OX_{10}]^{4-}$ system (with the infrared inactive potassium cation). From the possible 39 vibrations only 7 are infrared-active, belonging to the triply degenerate representation T_2. The representation of all vibrations contains:

$$\Gamma = 3A_1 + 3E + 3T_1 + 7T_2$$

An assignment of infrared bands via a normal coordinate analysis was not possible since the amount of data is unsufficient. Recording of Raman spectra with a Laser Raman spectrograph was not possible because of too much absorption at the position of the excitation energy.

In the spectrum of $K_4Cu_4OCl_{10}$ there is a triply split band around 560/cm, which must thus be associated with the central oxygen.[1] This Cu_4O stretching vibration is very intense and is absent in any other simple copper complex and can thus be taken as diagnostic for the presence of this structure type, as there is only little variation with axial ligands. In cases of L being a very bulky ligand, the ν_{Cu_4O} is usually split or broadened.

If we compare the $[Cu_4OCl_{10}]^{4-}$ anion with the $[Cu_2Cl_6]^{2-}$ we find bridging and terminal chloride in both of them, the Cu–Cl(t) distances are rather si-

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(27) W. Ludwig and M. Textor, *Helv. Chim. Acta, 54,* 1143 (1971).

(28) R.A. Howard and P.D. Keeton, *Spectrochim. Acta, 22,* 1211 (1966).

(29) H.P. Brehm, Ph.D. Thesis, Univ. of Frankfurt, 1970.

Table V. Infrared frequencies (below 600 cm^{-1}) of tetranuclear copper complexes Cu$_4$OX$_6$L$_4$.

Nr.	Cu$_4$OX$_6$L$_4$ X	L	Frequencies (cm^{-1})
I	Cl	pyridine	578(ss); 435(m); 256(ss); 242(s); 202(s); 120(w); 78(m)
II	Cl	2-picoline	599(s), 572(ss), 553(m); 481(m); 444(w), 436(m); 398(m); 265(sh), 251(ss), 230(sh), 194(w); 176(w); 114(w); 100(m)
XVII	Cl	triphenylphosphine oxide	586(ss); 538(ss); 44(m); 300(m); 256(m); 239(s), 220(sh); 170(m), 149(w); 120(m)
XVIII	Br	pyridine	534(ss); 439, 435(m); 238(sh), 223(s), 205(m); 167(w), 146(s), 133(sh); 106(w); 55(m), broad.
XIX	Br	2-picoline	564(s), 538(ss), 530(s); 479(m); 441, 434(m); 394(m); 250(sh), 236(m); 214(w), 198(s), 176(sh); 150(w); 139(m); 86(w); 72(w)
XIV	Cl	dimethylsulfoxide	583(ss); 490(s); 418(w); 340(m); 323(w); 250(sh), 244(s), 232(sh); 200(m); 140(w), broad; 97(w), broal.
XXX	Br	dimethylsulfoxide	548(ss); 484(m); 336(m), 320(sh); 203(m); 174(m); 136(m); 70(w), broad.
XLI	Cl	dimethylformamide	583(ss); 422(w); 405(m); 381(m), 240(ss); (198(w); 152(w)
XLII	Br	dimethylformamide	554, 550, 543(ss); 419(w), 405(m); 375(m); 193(ss); 130-150(s), broad.
XXXIII	Cl	chloride (potassium)	567, 554, 546(ss); 306(m); 293(ss); 242(m), broad; 205(w); 147(m), 103(m)
XXXIV	Cl	chloride (potassium)	552(ss); 304(sh), 288(ss); 235(m); 170(broad); 115(w), broad.
XXXV	Cl	chloride (ammonium)	543(ss); 460(w); 313(sh), 285(ss); 223(broad), 210(sh); 136(m); 122(m); 70(w), broad.
XXXVL	Cl	chloride ((CH$_3$)$_4$N$^+$)	534(ss); 458(w); 304(sh), 278(ss); 229(ss); 195(w); 168(w), 120(m); 72(w)
XXXVIII	Br	bromide ((CH$_3$)$_4$N$^+$)	517(s); 458(w); 275(w); 222(m); 204(sh), 190(sh); 172(m); 104(m).

milar.[9,31] In the latter the Cu–Cl(t) stretching vibration appears just above 300/cm, while as expected the Cu–Cl(μ) vibration is at lower frequencies.[33] For the anions XXXIII, XXXIV and XXXV with terminal chloride we find a strong band at 290/cm, while in the neutral complexes the first band assignable to the Cu–Cl(μ) absorption appears at 250/cm.[18,25,30] In the bromo compounds this bands is found slightly below 200/cm. The 250/cm band in the chloro series is sometimes accompanied by shoulders or it is—like the 200/cm band for most bromo compounds—unresolved and broad.

We showed above that for the tetrahedral molecule Cu$_4$OX$_6$L$_4$ (with L a point mass) there are seven IR-active vibrations, all of which are of presentation T$_2$, like the Cartesian coordinates. A simple description of the triply degenerate vibrations can be given which considers but one of the coordinates.

The system Cu$_4$OX$_5$L$_4$ contains four independent sets of atoms: The central oxygen (O), the four copper atoms (Cu), the bridging halides (X) and the ligand's coordinating atom (L). Along one axis there are two possible movements designed with + (parallel) and – (antiparallel). Thus the movements of all atoms can be described as the variation with repetition V$_R$ of two elements n (these are: + and –) to the fourth class p (four sets of atoms):

$$V_R^p(n)=n^p=2^4=16$$

Any two of these are equivalent (because + and – can be interchanged), thus leaving eight independent movements, which are summarized in Table VI. One of these is of course a translational movement, the other seven are related to the seven normal vibrations.

Table VI. Characterization of movements of type T$_2$ relative to one Cartesian axis.

O	Cu	L	X	characterization
+	+	+	+	translation
+	—	—	—	Cu-O stretching
+	+	—	—	L-Cu-X deformation
+	—	+	—	Cu-O-Cu deformation
+	—	—	+	Cu-X stretching
+	—	+	+	L-Cu-X deformation
+	+	—	+	Cu-L stretching
+	+	+	—	Cu-X stretching

Linear combinations of the relative movements of Table VI will give the normal vibrations, so the characterisation is only an indication of which force constant dominates.

Although the interchange of chloride and bromide in the axial and equatorial positions (relative to copper) might give further information, the resolution of spectra was unsufficient in the far infrared to assign seven fundamentals with accuracy.

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