Reaction of 17 with CCl_4. The reaction was carried out as described in parts a and b above, but upon attempted distillation only a few drops of **30** (Tables I and II) was distilled. The residue in the flask was dissolved in CH_2Cl_2, crystallized by adding hexane, and identified as oligomeric $\{[CH_2{=}CHCH(SiMe_3)]P(Ph){=}N\}_n$ by ^{31}P NMR (δ −5.42) and elemental analysis. Anal. Calcd: C, 61.24; H, 7.71. Found: C, 61.62; H, 6.70.

Reaction of 1 and 2 with CCl_4. The reaction of **1** with CCl_4 was carried out as described in parts a and b above and also according to procedure b with freshly distilled hexane as a solvent. In each case as many as four major signals and several smaller signals were observed in the ^{31}P NMR spectra of the reaction mixtures. Vacuum distillation did not give any fractions containing a single pure compound. However, low yields of pure samples of **44** and **45** were obtained in dilute CH_2Cl_2 solutions. Typically, phosphine **1** (7.23 g, 32.7 mmol) and CH_2Cl_2 (32 mL) were placed in a 250-mL round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, and addition funnel. After the solution was cooled to 0 °C, CCl_4 (3.2 mL, 32.7 mmol) in CH_2Cl_2 (32 mL) was added dropwise. The mixture was warmed to room temperature and stirred for ca. 1 h. Solvent removal and distillation afforded **44**. A similar procedure using ca. twice as much CH_2Cl_2 was used to obtain **45**.

Thermal Decomposition of 46. A sample (3.95 g, 12.8 mmol) of **46** was placed in a heavy-walled glass ampule that was sealed under vacuum. Light brown solids formed after heating in an oven at 180 °C for 67 h. The ampule was opened, and Me_3SiCl (1.38 g, yield 97%) was removed under vacuum. A ^{31}P NMR spectrum of the crude material contained a large signal at δ 15.24 and a small one at δ 6.12. Recrystallization from hot CH_3CN gave pure crystals of the trimer $(Ph_2P{=}N)_3$ (mp 228-230 °C; ^{31}P (THF) δ 15.9).[20]

Acknowledgment. The authors thank the U.S. Office of Naval Research, the U.S. Army Research Office, and the Robert A. Welch Foundation for generous financial support of this research.

Supplementary Material Available: Tables of ^1H and ^{13}C NMR spectroscopic data and analytical data for all new compounds (15 pages). Ordering information is given on any current masthead page.

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Structural Approach to the Behavior of ClO_4^- as a Ligand in Transition-Metal Complexes Using EXAFS, IR, and Raman Spectroscopy. 1. A Perchlorate-Bridged Copper Chain with Short Copper–Copper Distances in $Cu(ClO_4)_2$

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Received June 10, 1983

A new synthetic route has been applied to the preparation of anhydrous copper perchlorate and a combined study including extended X-ray absorption fine structure (EXAFS), infrared, and Raman spectroscopies used in an effort to determine the mode of coordination about copper. Oxygen atoms of the perchlorate groups form a square-planar environment around copper, with a short (1.96 Å) Cu–O distance, while oxygen atoms at a longer distance (2.68 Å) complete its coordination shell. The best agreement in the treatment of the EXAFS data is obtained by including a copper–copper contribution to the second coordination shell, so it is proposed that the perchlorate groups bridge two coppers, forming infinite chains. In one of these, the inter-copper distance is remarkably short (3.01 Å). However, no magnetic coupling has been found from either ESR or magnetic measurements between the two copper centers.

Until quite recently little information concerning the coordinating ability of the perchlorate group to metal ions was available in the literature.[2] Among the early studies is the work of Hathaway,[3] who recognized the presence of bidentate perchlorate in $Cu(ClO_4)_2$.

During the past decade, new synthetic methods have allowed the preparation of a series of perchlorato complexes of transition and non transition metals.[4,5] Unfortunately, such compounds exhibit a violent reactivity that limits considerably their manipulation. In particular, this reactivity prevents the employment of the solvents usual in crystal growth. For this reason, a solid product is frequently obtained in the form of a polycrystalline powder so that most of the structural data available to date have been obtained from vibrational spectroscopic studies. However, recent attempts to grow single crystals of perchlorato complexes of tin[6] and antimony[7] using $SbCl_5$ and $SnCl_4$ as solvents have been successful and have allowed their full structure determination by X-ray diffraction.

Extended X-ray absorption fine structure (EXAFS) is a powerful technique particularly well adapted to the structural study of polycrystalline powders, giving radial distances and information about the type and number of scattering atoms

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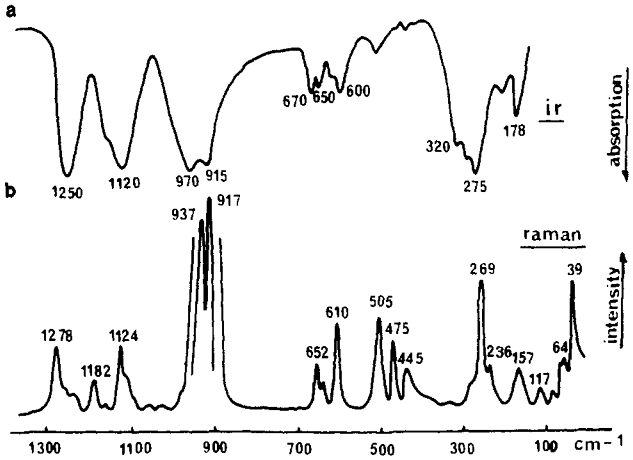

Figure 1. Vibrational spectra of $Cu(ClO_4)_2$: (a) infrared; (b) Raman.

and their motion relative to the absorber. This method has been developed at several synchrotron radiation sources, including LURE at the University of Paris-Sud, France.

We present here a new synthetic method for the preparation of $Cu(ClO_4)_2$ and the results of a combined study by conventional spectroscopy and by EXAFS of copper(II) perchlorate, from which we have obtained the precise structural data essential for a better understanding of the coordinating properties of the perchlorate group. Since EXAFS is still, as yet, a relatively uncommon experimental technique compared with, for example, X-ray diffraction, we present also the results of an EXAFS study of $CuCl_2 \cdot 2H_2O$ in order to check the validity of the method against known precise structural data.

Experimental Section

A. Synthesis. The preparation of $Cu(ClO_4)_2$ involved the general method previously described for the synthesis of anhydrous metal perchlorates.[4] Anhydrous or hydrated copper(II) chloride was allowed to react with a large excess of Cl_2O_6. (Methods of preparation, purification, and handling of Cl_2O_6 have already been reported.[4a]) Removal of the excess of Cl_2O_6 under vacuum gave a solid product identified as $(ClO_2)[Cu(ClO_4)_3]$. This orange solid was heated at 65–75 °C for 3 h, and the resulting light blue solid was characterized as $Cu(ClO_4)_2$ by classical analytical methods and X-ray powder diffraction. It should be noted that although the powder diffraction pattern is of good quality, its complexity does not allow a unique space group determination and, furthermore, prevents any profile refinements. The properties of this compound appear to be identical with those given by Nikitina and Rosolovskii[8] and by Hathaway and Underhill[3] for $Cu(ClO_4)_2$. Rosolovskii and co-workers have reported a crystalline modification with a transition at 150–160 °C. We have observed only an irreversible change in color from light blue to light green on heating to 170 °C, but otherwise the physical characteristics of the compound remain unchanged.

B. Spectral Measurements. Infrared. Copper(II) perchlorate is hygroscopic, and special care was taken by handling only in a glovebox under an atmosphere of dry nitrogen. Infrared spectra of the finely ground $Cu(ClO_4)_2$ were taken at room temperature by using silicon windows on a PE180 spectrometer. Spectral resolution was 1–5 cm^{-1} at 1400 cm^{-1} and 7 cm^{-1} at 300 cm^{-1}.

Raman. Raman spectra were recorded with a Dilor spectrometer and the data processed through a Tracor TN1710 modular multichannel computer (Northern Instruments). A Spectraphysics argon laser was used (5145 Å, 150 mW). The samples were sealed in Pyrex tubes and either were cooled to 180 K or were placed in a rotating cell at room temperature, in order to avoid decomposition. The resolution was 0.5–1.0 cm^{-1} over the entire spectral range.

Electronic Spectra. The spectrum of a powdered sample of $Cu(ClO_4)_2$ in the visible–UV region was recorded by using the technique of diffuse reflectance on a Beckman DK2A spectrometer, employing a Teflon cell with quartz (Infrasil) windows.

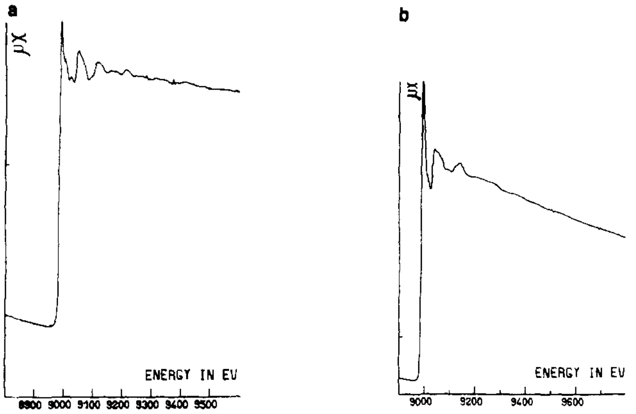

Figure 2. X-ray absorption spectra at 77 K of $\mu(\chi)$ vs. E showing the structure near the copper K edge: (a) $CuCl_2 \cdot 2H_2O$; (b) $Cu(ClO_4)_2$.

ESR Spectra. X-Band ESR spectra were taken at 77 K on a Bruker ER200D spectrometer. Samples were sealed in 5-mm Pyrex or quartz tubes.

EXAFS. Samples were prepared by grinding to a fine powder and mixing with dry paraffin oil. Thin films of the mull were sealed in stainless-steel holders having Kapton or Parafilm windows. This method of handling does not allow complete control of the homogeneity of the samples since pinholes and cracks may develop in the film, leading to uncertainty in the derived amplitudes.

The EXAFS spectrum of copper chloride dihydrate was obtained by using the same experimental procedure.

X-ray absorption spectra were recorded at 77 K by using the synchrotron radiation source DCI at LURE, on the EXAFS 1 setup described elsewhere.[9]

In each case, a complete spectrum was obtained from the averaging of several runs. The spectra $\chi(\mathbf{k})$ vs. the photoelectron wave vector, $\mathbf{k}$, were derived from the experimental $\ln (I_0/I)$ vs. photon energy, E, spectra. The raw spectra in Figure 2 show anomalies ("glitches") for certain orientations of the monochromator when multiple Bragg diffractions occur simultaneously. Two different monochromators (Si and Ge) were used in the experiments, so that the positions of the glitches are not coincident in Figure 2a,b. The spectra were corrected by removing the data points suffering from the glitches and subsequently interpolating using a cubic spline routine. After a preliminary selection of the energy threshold, E_0, the data were subsequently analyzed by using Fourier transform, Fourier filtering, and least-squares curve fitting.

These, now standard, techniques have been extensively described in the literature.[10] Theoretical amplitude and phase shift functions of each shell were taken from Teo, Lee, and co-workers.[11] The nonlinear fitted parameters are as follows: R_i, the absorbing atom–neighbor distance for the ith shell; σ_i, a damping coefficient related to thermal and static disorder; N_i, the number of atoms in the ith coordination shell; $(\Delta E_0)_i$, modification term for the a priori selected energy threshold for the ith shell. The EXAFS analysis programs were adapted at the Centre National Universitaire Sud de Calcul (CNUSC) from the software developed by J. Goulon (Nancy) and A. Michalowicz (Orsay).

Results and Discussion

Electronic and ESR Spectra. The room-temperature electronic spectrum of $Cu(ClO_4)_2$ exhibits a maximum at 11 900 cm^{-1} with shoulders at 7250 and 9350 cm^{-1}. The electron paramagnetic resonance gives a 3-g value spectrum with relatively sharp lines with no temperature dependence down to 77 K ($g_1 = 2.09$, $g_2 = 2.22$, $g_3 = 2.32$). These results are consistent with an axial type structure with probably a $d_{x^2-y^2}$

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ground state in either an elongated rhombic symmetry or an elongated axial symmetry with slight misalignment of the principal axes.[12]

Infrared and Raman Spectra. $Cu(ClO_4)_2$ and its hydrates have often been used as models to illustrate the bonding arrangements of ClO_4; however, their crystal structures are largely unknown, and owing to the lack of Raman and low-frequency IR data, the analysis of their vibrational spectra is still incomplete.

We present here for the first time the Raman spectrum of $Cu(ClO_4)_2$ in the mid- and low-frequency regions and the results of an extended IR analysis to include the range 350–200 cm^{-1} where the stretching and bending vibrations involving the copper–oxygen framework are expected. The experimental Raman and IR spectra are shown in Figure 1.

The IR spectrum of $Cu(ClO_4)_2$ has previously been reported by Hathaway and Underhill[3] and by Rosolovskii and co-workers.[8] Both studies report the presence of a band at 1030 cm^{-1}, which is absent in our spectra. It is possible that this band arises from hydration of the sample; significantly an intense band at 1030 cm^{-1} is present in the IR spectrum of $Cu(ClO_4)_2{\cdot}2H_2O$.[13]

Depending on its coordination to the metal atom, the local symmetry of the perchlorate group is reduced from T_d in the perchlorate ion to C_{3v} in monodentate perchlorate or to C_{2v} or C_s in a bidentate perchlorate group. As a result of these changes in symmetry, the IR spectra of the perchlorate group will be different, depending on the mode of coordination. According to Hathaway and Underhill,[3] four bands or groups of bands are expected for the stretching vibrations of bidentate perchlorate whereas only three such bands are expected for a monodentate group. The IR spectrum presented here is characteristic of a compound containing bidentate perchlorate.

The analysis of the vibrational spectrum, including the Raman, is more complicated than initially expected from the mid-frequency IR data. A total of eight resolved bands are observed in the range 1300–800 cm^{-1}. Despite the possibility of intermolecular coupling and the isotopic effect, which could lead to band splitting and hence to more bands than expected, from our experience of the vibrational spectra of other solid perchlorates[6,7] it appears that such effects are minimal.

The number of bands thus suggests the existence of at least two different types of perchlorate group. It may be noted that the lowering of the frequencies due to coordination is much less than in the case of perchlorate coordinated to a post transition element, although the strength of the perchlorate–metal interaction is comparable.[6,7]

In the region below 400 cm^{-1}, $Cu(ClO_4)_2$ gives rise to a complex spectrum. A similar complexity is found in the low-frequency region of the IR spectra of anhydrous transition-metal nitrates in which the strong covalent interaction between the nitrate group and the metal atom produces bands in the range 400–200 cm^{-1}, assigned to metal–oxygen stretching vibrations.[14] For example, a broad IR absorption at 336 cm^{-1} is observed for $Cu(NO_3)_2$ where Cu–O distances as short as 1.94 Å have been found from a single-crystal X-ray diffraction study.[15]

On the basis of the infrared and Raman data, regular square-planar or octahedral coordination geometries around copper can be excluded. In IR and Raman spectra, D_{4h} and O_h geometries give rise to similar band patterns: only one mode is active in IR whereas two are expected in Raman. The number of bands observed experimentally for $Cu(ClO_4)_2$ does not conform to either symmetry. Although some bands appear at identical frequencies in both the Raman and IR spectra, four distinct bands are found in IR and five may be resolved in Raman, so it may be concluded that the structure around copper is far from regular D_{4h} or regular O_h and that, in addition, the coordination at copper involves more than four oxygen atoms.

It is interesting to note that in the nitrate analogue[15] the copper atom has a coordination that may be represented as (4 + 1 + 1) or as (4 + 2) in which four oxygen atoms are arranged in a square-planar fashion around the central copper with short (1.94–2.01 Å) Cu–O distances and the two remaining oxygens are found above and below this plane with longer and not necessarily equal Cu–O distances (2.65–2.43 Å). Interpretation of the IR spectrum of $Cu(ClO_4)_2$ according to such a coordination scheme leads to the following assignments: the higher frequency bands (335, 290, 265 cm^{-1}) to stretching vibrations of the short Cu–O bonds and those at lower energies (210, 237 cm^{-1}) to stretching of the weaker interactions.

Results of the EXAFS Experiment. X-ray absorption spectra at 77 K of $Cu(ClO_4)_2$ and $CuCl_2{\cdot}2H_2O$ showing the extended fine structure beyond the K absorption edge of copper are given in Figure 2. The absorption coefficient is shown as a function of the energy of the X-ray photons. E_0 is defined as the energy corresponding to the second maximum of the derivative of the absorption coefficient with respect to the energy at the edge.

Plots of the EXAFS function $\chi(\mathbf{k})$ vs. $\mathbf{k}$ at 77 K for the extended fine structure are shown in Figure 3. The associated Fourier transforms of the function $\mathbf{k}^3{\cdot}\chi(\mathbf{k})$, which were taken over the range of wave vectors up to $\mathbf{k}$ = 13 $Å^{-1}$, are shown in Figure 4.

The function $\mathbf{k}^3{\cdot}\chi(\mathbf{k})$ determined from the best fit of the structural parameters to the known values of the function, obtained by inverting the Fourier transform of the EXAFS data over a range of R between 1.0 and 3.8 Å to include the major peaks in the Fourier transform, is shown in Figure 5. Since treatment by least-squares curve fitting involved at least four coordination shells and 20 parameters, the refinement procedure was carried out in two steps. First, each of the main peaks in the Fourier transform was filtered, and the relevant parameters, R, σ, E_0, and the number of nearest neighbors, were refined (using a scale factor common to all the shells). The second step involved the refinement of only the number of nearest neighbors, and the damping factor, σ, for all the shells to 3.8 Å treated together. R and ΔE_0 were held fixed to their values obtained in the fitting of each shell separately. The final refinements thus involved fitting of eight parameters, and the results are presented in Table I.

Copper(II) Chloride Dihydrate. This was used as an experimental control to check the transferability of the phase shift and amplitude functions of Teo, Lee, and co-workers.[11] The precise structure of $CuCl_2{\cdot}2H_2O$ has been determined at room temperature by Engberg,[16] and this result is compared with those obtained from EXAFS in the table. It may be seen that, as usual, phase-shift transferability is good, since there is reasonable agreement in the bond lengths; the slight difference can be accounted for by a contraction in the direction of the b axis due to the lower temperature of the EXAFS experiment. For the amplitude functions the transferability is not as satisfactory although the number of nearest neighbors in each case is always within one atom of that expected. Such amplitude problems are not unexpected owing to sample inhomogeneity as discussed in the Experimental Section.[17] The fitted coordination numbers should therefore be taken as relative rather than absolute values.

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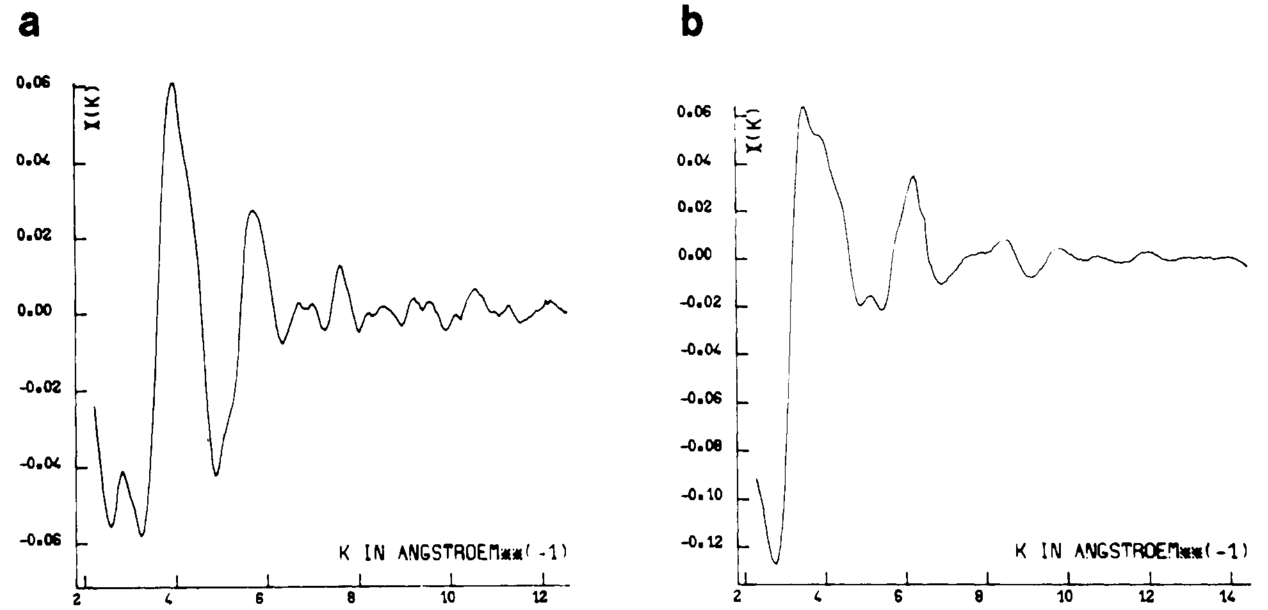

Figure 3. k-Space EXAFS spectra after background removal and conversion to photoelectron wavenumbers ($\chi(\mathbf{k})$ in arbitrary units vs. $\mathbf{k}$ in $Å^{-1}$): (a) $CuCl_2 \cdot 2H_2O$; (b) $Cu(ClO_4)_2$.

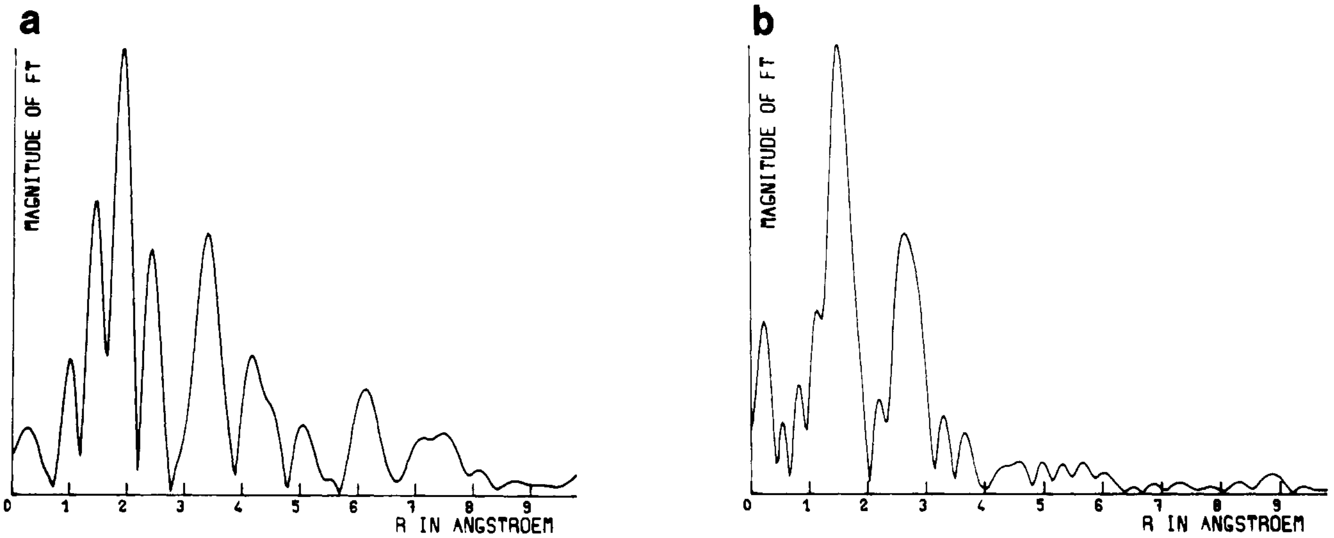

Figure 4. Fourier transform of the weighted EXAFS spectrum in R space ($\mathbf{k}^3\chi(\mathbf{k})$ in arbitrary units vs. R in Å): (a) $CuCl_2 \cdot 2H_2O$; (b) $Cu(ClO_4)_2$.

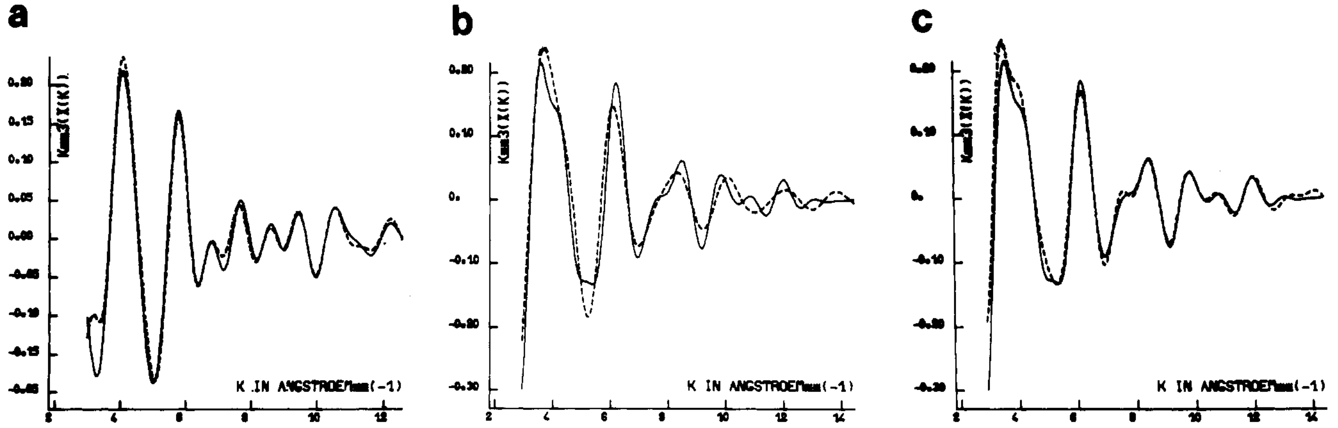

Figure 5. k-Space-filtered spectra (solid line) with the corresponding calculated curves (dashed line): (a) $CuCl_2 \cdot 2H_2O$; (b, c) $Cu(ClO_4)_2$. In (b) the copper contribution has been removed from the second shell to show its relative importance in the spectrum. The quality of the fit as estimated from the residual factor $\rho = \sum_k(\chi_{\text{exptl}} - \chi_{\text{calcd}})^2/\sum_k\chi_{\text{exptl}}^2$ is (a) 3%, (b) 17%, and (c) 2%.

Copper(II) Perchlorate. The strongest peak in the Fourier transform of the EXAFS oscillation in $Cu(ClO_4)_2$ (Figure 4b) is the signal from the first coordination shell around copper. Introducing the theoretical phase shift for oxygen, the observed peak position gives a copper–oxygen distance, R_{Cu-O}, of 1.96 Å, which is identical with that found in several copper(II)

Table I. First- and Second-Shell Fits for $Cu(ClO_4)_2$ and $CuCl_2 \cdot 2H_2O$

	shell	N_{EXAFS}[a]	N_{CRYST}	R_{EXAFS},[b] Å	R_{CRYST},[c] Å		Debye-Waller factor (σ^2),[a] Å^2	E_0,[b] eV
$CuCl_2 \cdot 2H_2O$	1st Cu-O	1.2 (3)[d]	2	1.94 (2)	1.94	1.94	0.0009 (12)	9001
	2nd Cu-Cl	2.0 (2)	2	2.30 (1)	2.28	2.29	0.0016 (8)	9001
	2nd Cu-Cl	2.1 (4)	2	2.88 (1)	2.91	2.94	0.0025 (20)	8995
	3rd Cu-Cu	3.0 (2)	2	3.70 (2)	3.70	3.76	0.0016 (8)	8991
$Cu(ClO_4)_2$	1st Cu-O	3.7 (4)		1.96 (1)			0.0009 (6)	9004
	2nd Cu-O	1.9 (8)		2.68 (3)			0.0064 (32)	8984
	2nd Cu-Cl	5.2 (9)		2.73 (2)			0.0225 (30)	9003
	2nd Cu-Cu	2.4 (3)		3.01 (1)			0.0025 (10)	9004

[a] Values of N and σ obtained by fitting the whole spectral range including all coordination shells, with E_0 and R constant. [b] Values obtained from a fit of each coordination shell treated separately after Fourier filtering. [c] The second column represents distances obtained by using the reported lattice parameters and atomic positions of ref 16; $a = 8.10$, $b = 3.76$, $c = 7.43$ Å. Better agreement is obtained by using a value of 3.70 Å for b, which could result from contraction of the cell on cooling (first column). [d] In each case the standard deviation in parentheses refers to the last significant figure.

complexes containing oxygenated ligands.[18]

Subsequent filtering of the peak and least-squares curve-fitting analysis confirmed the Cu–O distance to be 1.96 (1) Å with a damping coefficient, σ, of 0.033 (1) Å. σ reflects the thermal motion of the oxygen relative to the copper atom as well as the static spread of the Cu–O distances about 1.96 Å. From the low value of the Debye–Waller factor it may be assumed that the Cu–O distances in the first coordination shell are equal within 0.02 Å.

The shape of the second peak of the Fourier transform suggests that it is a composite signal, resulting from the overlap of several different features. It is reasonable to suppose that the shell at 2–3 Å includes the chlorine of the perchlorate group and that it might include oxygen atoms at a longer distance from copper.

Thus, in the curve-fitting analysis, the second shell was modeled by chlorine and oxygen atoms at similar distances from copper and with identical Debye–Waller factors. However, any attempt to fit the second shell with only chlorine and oxygen atoms invariably showed very poor agreement between the experimental and calculated curves and, hence, high residual factors.

For this reason, copper atoms were introduced into this shell in addition to chlorine and oxygen. A marked improvement in the fit was obtained (R = 3%), and the copper–copper distance refined to 3.01 (1) Å. Copper–chlorine and copper–oxygen distances were found to be 2.73 (2) and 2.68 (3) Å, respectively. (The chlorine atoms suffer from a high Debye–Waller factor (σ_d = 0.15 Å), which probably indicates a range of copper–chlorine interatomic distances.)

Owing to the problem associated with least-squares refinement of atomic parameters of atoms in close proximity, correlation coefficients and the derived standard deviations are high, especially for the N and σ of chlorine and oxygen.

It is to be noted that the copper–copper contribution is vital to the fit of the second shell. Figure 5b shows the effect of removing the Cu–Cu contribution on the fit of theoretical to the experimental data. Several other attempts to model the system using only the pairs Cu–O, Cu–Cu or Cu–Cl, Cu–Cu gave agreement factors that were not significantly different from that obtained by using the three-atom model. Nevertheless this latter model is chemically and spectroscopically sound.

Several conclusions can be drawn from the data in the table. First, a four-coordination geometry is present around copper with strongly coordinated perchlorate groups. It is generally thought that perchlorate is a poorly coordinating ligand, and in this respect the 1.96 Å metal–oxygen distance is the shortest to be reported for a perchlorato complex.

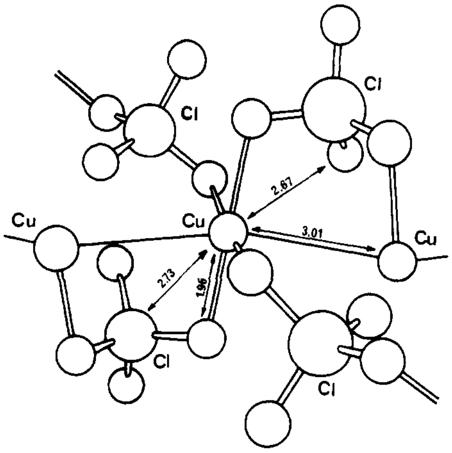

Figure 6. Proposed model for the copper chain with short Cu–Cu distances.

Second, the value of N for chlorine (5 ± 1) is consistent with the presence of four perchlorate groups surrounding each copper atom. It can be assumed, therefore, that each perchlorate bridges two coppers, producing infinite chains.

Third, each copper atom has two neighboring coppers at a short distance of 3.01 Å. Such a situation may be realized in one chain, with the interatomic distance being maintained by the perchlorate bridge (Figure 6). This demonstrates the ability of the perchlorate group to bridge metal atoms in such a way that a direct interaction between the metal centers is possible. Hence, it might play a similar role as carboxylate or sulfate ions in stabilizing metal–metal bonds. There is no evidence of longer Cu–Cu distances from the Fourier transform, which is relatively flat after 4 Å.

On this basis, the simplest model for $Cu(ClO_4)_2$ can be derived from the structure of copper(II) chloride,[19] in which chains of copper atoms are doubly bridged by two equivalent coordinated anions. However, owing to the size of the perchlorate group and the short Cu–Cu distance, such a situation is difficult to realize. Hence, we prefer a model with two types of nonlinear chain, one containing short Cu–Cu distances and the second with longer Cu–Cu distances, which might not be detected by EXAFS spectroscopy (Figure 6). This model is consistent with the existence of two different bidentate groups suggested by vibrational spectroscopy. In $CuCl_2 \cdot 2H_2O$, for a copper–copper distance of about 5.5 Å and a coordination number of 2, the resulting EXAFS signal is very weak. Furthermore, in the case of a linear chain, as in copper chloride like structures, multiple scattering effects (focusing)[20] could

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lead to the appearance of a peak corresponding to twice the Cu–Cu separation (that is, at ~6 Å), but no such signal is apparent in the Fourier transform of $Cu(ClO_4)_2$. On the other hand, such a peak enhanced by the focusing effect is observed for $CuCl_2{\cdot}2H_2O$ and also in the spectra of $CuCl_2$ and Cu_2O.[21]

The proposed structure resembles that of anhydrous copper sulfate, in which copper atoms are linked in infinite chains, with both short (3.35 Å) and long (4.84 Å) copper–copper distances, except that here two nonequivalent bridging sulfate groups maintain the shorter Cu–Cu separation, one bridge involving two oxygen atoms, Cu–O–S–O–Cu, and the other only one, Cu–O–Cu.[22]

A final remark arising from the EXAFS results concerns the short Cu–Cu distance in one chain, suggesting some kind of interaction, but the ESR spectrum shows no evidence of exchange interaction, in particular in the half-field region ($\Delta(ms) = \pm 2$). In most cases for complexes containing copper chains or dimers with copper–copper distances >2.8 Å, the magnetic interaction proceeds via an exchange mechanism through the bridging ligand, and the relative orientation of the magnetic orbitals is a key factor,[23] not only the intermetallic distance. In addition, magnetic measurements confirm the absence of any significant exchange coupling between the two copper centers and are thus entirely compatible with the ESR results.[24]

Acknowledgment. We thank Professor O. Kahn of the Laboratoire de Spectrochimie des Elements de Transition, Université de Paris-Sud, Orsay, for help with the magnetic measurements and for useful discussions. We gratefully acknowledge the help of the staff of the Laboratoire de l'Accélérateur Linéaire, Orsay, who operated the storage ring D.C.I. and Dr. J. Goulon (University of Nancy, France) for his help in programming. D.J.J. thanks the Royal Society of Great Britain and the French CNRS for the award of a European Exchange Fellowship.

Registry No. $Cu(ClO_4)_2$, 13770-18-8.

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Synthesis and Structure of $Co_6(\mu_6\text{-}C_2)(\mu\text{-}CO)_6(CO)_8(\mu_4\text{-}S)$: First Example of a Peripheral Dicarbide Metal Carbonyl Cluster

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Received June 30, 1983

As the sixth fully characterized member of the $C_vS_wCo_x(CO)_y$ family of cluster carbonyls, the title compound (VI) has been isolated as a new product in the reaction of $Co_2(CO)_8$ with CS_2 at ambient temperature under an N_2 atmosphere, in low yield (ca. 5% relative to the sum of soluble carbonyl products). Its structure has been characterized by X-ray diffraction analysis and IR spectroscopy. Crystal data: space group $P2_12_12_1$ (D_2^4, No. 19), $a = 18.618$ (5) Å, $b = 13.528$ (5) Å, $c = 9.151$ (4) Å, $Z = 4$, $d_{\text{calcd}} = 2.31$ g cm^{-3}. The structure was solved by using a combination of the conventional Patterson method with difference Fourier techniques. Refinement on 1509 reflections for which $F > 6\sigma(F)$ resulted in the final residuals $R = 0.045$ and $R_w = 0.044$. The structure consists of a "boat" array of six cobalt atoms, of which the four basal ones form an essentially regular square, metal–metal bonded along all four edges. The two apical cobalt atoms are connected through a Co–C–C–Co array. The two carbon atoms of the "peripheral" dicarbido unit are bonded also to the four basal cobalt atoms. These four atoms, in turn, are capped also by a face-bridging μ_4-sulfur atom. Each of the six peripheral Co–Co bonds bears μ-carbonyl ligand, five of them showing different amounts of asymmetry. The solution IR spectrum suggests a dynamic behavior over all six bridges whereas the solid-state IR spectrum reflects the unique situation of the single symmetrical bridge. The apical cobalt atoms bear two of the eight terminal carbonyls, and one CO is terminally bonded to each of the four basal metal atoms. When treated with carbon monoxide, complex VI loses the sulfur atom to yield $(CO)_9Co_3C_2Co_3(CO)_9$, which was also directly observed among the products of the reaction of dicobalt octacarbonyl with CS_2.

Introduction

Transition-metal carbido clusters have recently been reviewed.[1] The authors divided these clusters into two main classes according to the structural features, i.e. the "cage carbides", in which the metal polyhedron completely encloses the carbido carbon atom, and the "peripheral carbides", in which the carbon atom is bonded at the periphery of the metal polyhedron, generally leaning out of a face of the metal framework.

Even if in the last 2 years there has been an increase in the number of carbido metal clusters reported, reaching at present ca. 100, very few examples among them are dicarbido clusters, i.e. complexes containing two carbido carbon atoms. All the dicarbido metal carbonyl clusters hitherto reported are cage carbides and can be divided into two types:[2] (i) where a C_2 unit is encapsulated in a metal polyhedron, as $Rh_{12}(C_2)(CO)_{25}$[4] and $[Co_{11}(C_2)(CO)_{22}]^{3-}$[5] and (ii) where two separate carbido

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[2] In principle, the complex $(CO)_9Co_3C_2Co_3(CO)_9$[3] can belong to the carbido family, as the C_2 unit is bonded only to metal atoms, so being considered the unique member of a third type of dicarbido clusters, in which C_2 links two separate polymetallic entities.

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