$^{34}SO_2F$, SiF_3,[12] 2.0; ~310, $C(OSO_2F)_3^+$, 1.5. F_3COSO_2F: 47, COF^+, 4.0; 48, SO^+, 2.3; 64, SO_2^+, 1.3; 67, SOF^+, 2.6; 69, CF_3^+, 100.0; 70, $^{13}CF_3^+$, 1.3; 83, SO_2F^+, 16.1; 85, $^{34}SO_2F^+$, SiF_3^+, 1.0. It is observed that the ion corresponding to mass number 47, COF^+, increases in the expected manner as the number of oxygen atoms bound to a single carbon increases. The SO_2F^+ ion is generally of high intensity in these as well as other reported O-fluorosulfate compounds.[10,13]

The reaction between $S_2O_6F_2$ and CBr_4 using a 2:1 molar ratio gave product results similar to those reported by Shreeve,[4] who used CCl_4 as the substrate, *i.e.*, CO_2 and $S_2O_5F_2$. These were produced in nearly a 1:2 molar ratio. However, in the case involving CBr_4 a trace quantity of another compound was isolated which may have the structure $O{=}C(OSO_2F)_2$. This compound slowly decomposed to yield equimolar quantities of CO_2 and $S_2O_5F_2$. In the mass spectrometer using a heated cycloid tube only CO_2 and $S_2O_5F_2$ were observed, again in equimolar quantities. The infrared spectrum of this compound showed a band in the carbonyl region at 1886 cm.$^{-1}$ and absorptions at 1504, 1266, 847, 758, and 708 cm.$^{-1}$ which are frequencies characteristic of the $-OSO_2F$ group. Other bands at 1136 and 1028 cm.$^{-1}$ are unassigned. The ^{19}F n.m.r. spectrum shows one singlet resonance at $-51.6\ \phi$ in the SF region of the fluorosulfate group. Pyrosulfuryl fluoride has one resonance at $-47.2\ \phi$. The compound was never obtained in a pure state so no further analysis was attempted.

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The Metal–Metal Bond in the Copper(II) Acetate Dimer. Nuclear Magnetic Resonance Evidence for a δ Bond

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Considerable uncertainty seems to exist concerning the nature of the Cu–Cu interaction in the copper acetate complex, $Cu_2(C_2H_3O_2)_4\cdot 2H_2O$. That a relatively strong interaction takes place is indicated by the Cu–Cu distance of 2.64 Å.[1] and by the singlet character of the ground state.[2] However, the nature of this interaction seems to be the subject of some disagreement. Arguments based on theoretical calculations, on the visible spectrum, and on the electron spin resonance spectrum have been advanced for a σ bond[3] and for a δ bond.[4]

In essence the problem reduces to finding the relative order of the three highest energy molecular orbitals derived from the d orbitals of the two copper atoms. It is generally agreed[3,4] that these three orbitals are the a_{2u} (σ^*) molecular orbital derived from the d_{z^2} atomic orbitals which lie along the Cu–Cu axis and the b_{1g} (δ) and b_{2u} (δ^*) molecular orbitals derived from the $d_{x^2-y^2}$ atomic orbitals which lie normal to the Cu–Cu axis. The three possible arrangements of these molecular orbitals are

—b_{2u} (δ^*)	—b_{2u} (δ^*)	—a_{2u} (σ^*)
—b_{1g} (δ)	—a_{2u} (σ^*)	—b_{2u} (δ^*)
—a_{2u} (σ^*)	—b_{1g} (δ)	—b_{1g} (δ)
A	B	C

Since there are four electrons to place in these three orbitals, the highest energy orbital will be vacant in the ground state. Thus orders A and B, where the δ^* orbital is vacant and the σ^* orbital is filled, correspond to the formation of a δ bond between the two copper atoms while order C, where the σ^* orbital is vacant and the δ^* orbital is filled, corresponds to a σ bond. Order A is favored by Ross and co-workers,[4] while order C has been suggested by Forster and Ballhausen.[3] The purpose of this report is to present some single crystal nuclear magnetic resonance results which seem to strongly support order B.

The nuclear quadrupole splitting of the nuclear magnetic resonance of a nucleus with a spin greater than $^1/_2$, $I > {}^1/_2$, is dependent upon the nonspherical components of the electric field gradient tensor, V_{ij}, at the site of the nucleus.[5] The single crystal n.m.r. spectrum of a material which contains such a nucleus thus gives some information about the electronic structure of the material.[6]

In the case at hand, the quadrupole splitting of the copper-63 resonance, $I = {}^3/_2$, should give some information about the electronic distribution in the copper acetate dimer. If the difference between the component of the electric field gradient tensor along the Cu–Cu axis, $V_{\mathrm{Cu,Cu}}$, of the dimer in the ground state and in the lowest triplet state can be determined, it should be possible to tell which of the three orders given above is the correct one. In order A the ground state, $(a_{2u})^2(b_{1g})^2$, and the triplet state, $(a_{2u})^2(b_{1g})(b_{2u})$, should have essentially the same electron density along the Cu–Cu axis because both b_{1g} and b_{2u} contain a nodal axis corresponding to the Cu–Cu axis. Thus $V_{\mathrm{Cu,Cu}}$ should be essentially the same in the two states. Since only the traceless portion of the tensor can be measured, there might be a small increase in the measured value for the triplet due to a slight decrease in the components of the tensor normal to the Cu–Cu axis, but the effect should be small.

In order B, the transition from the ground state to the triplet state corresponds to transferring one electron from the a_{2u} orbital which lies along the Cu–Cu axis to the b_{2u} orbital which has no electron density along this axis. Thus the electron density along the Cu–Cu axis should be smaller and the electron density

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normal to this axis should be greater in the triplet state than in the singlet state. The measured value of $V_{\mathrm{Cu,Cu}}$ should therefore be considerably smaller in the triplet than in the singlet. In order C, the electronic change is just the reverse of order B leading to a larger value for $V_{\mathrm{Cu,Cu}}$ for the triplet than for the singlet.

The relative populations of the two levels can be varied by varying the temperature (the triplet lies about 286 cm.$^{-1}$ above the singlet), and the singlet–triplet transition should be rapid enough that an average signal will be observed. Thus the determination of the temperature dependence of the quadrupole splitting of the copper-63 resonance should supply the information necessary for a choice among the three possible arrangements of the energy levels.

Results and Discussion

Preliminary experiments showed that the copper-63 resonance in a single crystal of copper(II) acetate could be detected up to a temperature of approximately 160°K. with the apparatus available. Above this temperature the signals became too weak to be detected with certainty due to the increasing paramagnetism of the crystal. Below this temperature, the outer two lines of the three-line pattern could be detected readily, but the position of the central line could not be determined accurately due to interference from metallic aluminum-27 and copper-63 in the probe. The individual lines where approximately 20–30 gauss wide and showed some evidence of the expected spin–spin splitting. The weaker copper-65 resonances could also be seen at lower temperatures, but since they would yield no additional information, they were ignored.

Rotation of the crystal at 100°K. indicated that, as anticipated, the principal axis of the electron density gradient coincides with the Cu–Cu axis in the dimer within the limits of error of the measurement. Two identical patterns separated by 69° arising from the two sites in the unit cell were observed.

Since the two patterns were identical and since in single crystal spectra of this type the patterns arising from different sites are completely independent, only the lines arising from one site need to be considered. The crystal was then oriented so that the principal axis of the site under consideration was parallel to the magnetic field. The positions of the outer two lines corresponding to that site were then determined at several different temperatures without moving the crystal, with the results shown in Table I.

The line separations clearly decrease with increasing temperature indicating that the quadrupole splitting in the triplet state is smaller than in the ground state. Assuming a linear relationship between the fraction triplet and the splitting measured from the calculated center line position of 3862 gauss, the best least-squares value for the splitting in the pure singlet state and in the pure triplet were found to be 198 ± 2 gauss and 130 ± 2 gauss, respectively. These values correspond to quadrupole coupling constants,[5] e^2qQ, of

$$e^2qQ\ (\text{singlet}) = 2.19 \pm 0.02\ \text{Mc./sec.}\ (10\ \text{kgauss})$$
$$e^2qQ\ (\text{triplet}) = 1.46 \pm 0.20\ (\text{estd.})\ \text{Mc./sec.}\ (10\ \text{kgauss})$$

The value for the triplet is rather uncertain due to the long extrapolation involved, but it is definitely considerably lower than the value for the singlet.

TABLE I

QUADRUPOLE SPLITTING OF COPPER-63 AT VARIOUS TEMPERATURES (FREQUENCY 4.30 MC./SEC.)

Temp., °K.	Fraction triplet[a]	High-field line, gauss	Low-field line, gauss	Center line calcd.[b]
156	0.136	4052 ± 3	3676 ± 3	3864
148	0.119	4051 ± 2	3670 ± 2	3861
117	0.059	4055 ± 2	3667 ± 2	3861
77	0.010	4060 ± 1	3666 ± 1	3863
				Av. 3862

[a] Calculated for an energy difference of 286 cm.$^{-1}$ between the singlet and the triplet. [b] In this orientation, the center line should be exactly midway between the two outer lines.

These values for the coupling constants are considered to be minimum values because any error in the alignment of the principal axis of the site with the magnetic field would reduce both of the coupling constants by the factor $(3\cos^2\theta - 1)/2$, where θ is the angle between the principal axis and the field. However, such a possible misalignment will not change the ratio of the two coupling constants which is all that is needed to answer the question at hand. Thus the conclusion that the coupling constant of the singlet is greater than that of the triplet is independent of the orientation of the crystal at which the measurements were made.

A consideration of the changes in the population of the various vibrational levels with changes in temperature and the expected differences in geometry of the singlet and triplet states shows that neither of these effects would be expected to give rise to the observed change. The principal effect of changes in the average metal–ligand distance in the dimer due to changes in the population of the various vibrational levels would be to shift the entire pattern up- or downfield (the chemical shift) with only the anisotropic portion of this change affecting the coupling constant. Since the isotropic portion of this effect is too small to cause an appreciable shift in the center line, it would seem unreasonable to ascribe the observed change in the coupling constant to the anisotropic portion. In addition, if the metal–ligand frequencies are in the expected range of 400–500 cm.$^{-1}$, the changes in population of the various vibrational levels in the temperature range 70–160°K. should be very small.

The changes in geometry in going from the singlet to the triplet should be related to the electronic changes. For example in case B above, the transfer of an electron from the a_{2u} orbital to the b_{2u} orbital should lead to a slight decrease in the Cu–water distance and a slight increase in the Cu–acetate distance. This change in geometry will tend to reduce the difference between the coupling constants for the triplet and the singlet, but the coupling constant for the triplet should still be smaller. Only if we make the very unreasonable assumption that the change in geometry is so large that $V_{\mathrm{Cu,Cu}}$ actually increases as an electron is removed from this axis is any difficulty encountered. Similar arguments can be made for the other possible arrangements which show that the observed effects would not be expected to arise from this source.

Thus the results seem to be consistent only with order B of the levels given above.

Experimental

The crystal used was a cylinder approximately 10 mm. in diameter and 20 mm. long oriented with respect to the unit cell so that the Cu–Cu axes of both sites were normal to the cylinder axis. Since the orientation of the crystal was not critical, it was simply oriented manually using the external faces of the crystal and a protractor. The diameter was chosen to give a slip fit in the probe insert.

The spectra were taken with a Varian DP-60 spectrometer operating at 4.3 Mc./sec. The probe was fitted with a Varian 4331-TWL dewar probe insert cooled with liquid nitrogen. The only modification of the instrument was the replacement of the receiver gain control with a continuously variable resistor to permit operation at as high a gain as possible consistent with a reasonable base line. The spectra were recorded at maximum transmitter power, the sweep frequency was 40 c.p.s., and the scan rate was approximately 25 gauss/min.

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Stereospecific Reactions of Various *cis*- and *trans*-Bromobis(ethylenediamine)cobalt(III) Complexes with Chlorine[1a]

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It has been shown[2] that the reaction of $Co(NH_3)_5Br^{+2}$ with Cl_2 is rapid and results in the quantitative formation of $Co(NH_3)_5Cl^{+2}$

$$Co(NH_3)_5Br^{+2} + {}^1/_2Cl_2 = Co(NH_3)_5Cl^{+2} + {}^1/_2Br_2$$

In order to determine the stereochemistry of this type of reaction, the studies have been extended to complexes of the class *cis*- and *trans*-$Co(en)_2XBr^{+n}$ (X = NH_3, Cl, Br), and the results obtained are reported in the present paper.

Experimental

Preparation of Complexes.—*trans*-$[Co(en)_2Cl_2]Cl$ was prepared according to the method of Bailar[3] and was used as the starting material for the preparation of the other complexes. The following compounds were prepared as described in the references cited: *cis*-$[Co(en)_2NH_3Br]Br_2$,[4] *trans*-$[Co(en)_2NH_3Br]S_2O_6$,[5] *cis*-$[Co(en)_2Br_2]Br$,[6] *trans*-$[Co(en)_2Br_2]Br$,[7] *trans*-$[Co(en)_2Br]ClO_4$,[8] *cis*-$[Co(en)_2BrCl]Br$,[9] and *trans*-$[Co(en)_2BrCl]ClO_4$.[10] *cis*-$[Co(en)_2BrCl]ClO_4$ was obtained by treating a concentrated solution of the bromide salt with concentrated perchloric acid.

The purity of the complexes was ascertained by comparing the absorption spectra measured in the present work with the spectra reported in the literature. Table I lists the wave lengths of the first absorption maximum and the corresponding molar absorbancy indexes for the complexes investigated.

TABLE I

SPECTRAL DATA FOR $Co(en)_2XBr^{+n}$ COMPLEXES[a]

Complex	λ, mμ[b]	A[c]	Ref.
cis-$Co(en)_2NH_3Br^{+2}$	540	81.3[d]	This work
	540	81	*e*
trans-$Co(en)_2NH_3Br^{+2}$	545	51.6[f]	This work
	545	50	*g*
cis-$Co(en)_2Br_2^+$	550	115[h,i]	This work
	552	110	*j*
trans-$Co(en)_2Br_2^+$	655	51.6[h,k]	This work
	658	53.8	*j*
	648	45	*l*
	656	48.5	*m*
cis-$Co(en)_2BrCl^+$	542	98.2[h,i]	This work
	550	100	*n*
	548	96.3	*m*
trans-$Co(en)_2BrCl^+$	634	42.2[h,k]	This work
	640	41	*n*
	635	41.4	*m*

[a] Measurements at room temperature, unless otherwise indicated. [b] Wave length for first absorption maximum. [c] Molar absorbancy index at maximum. [d] Average of fourteen measurements. [e] R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956). [f] Average of four measurements. [g] M. L. Tobe, *ibid.*, 3776 (1959). [h] Measured at 13 ± 1°. [i] Single measurement. [j] M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **271**, 101 (1952). [k] Average of two measurements. [l] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956). [m] Ref. 8. [n] Ref. 10.

Resolution of *cis*-$[Co(en)_2NH_3Br]Br_2$ was achieved by precipitation as the D(+)-α-bromocamphor-π-sulfonate, as described by Werner.[11] Only the least soluble diastereoisomer, *d*-*cis*-$[Co(en)_2NH_3Br]$D(+)-$C_{10}H_{14}O_4BrS)_2$, was isolated. Four resolutions were carried out, but in no case was an optically pure material obtained. This was shown by a comparison of observed values of $[M]_D$ (for example +991, +940) with the value $[M]_D$ = +1058, calculated from the contributions of the cation[12] and anion.[13] However, since we were only interested in the question of retention or loss of optical activity upon reaction, the polarimetric studies were carried out with the partially resolved materials.

Hypochlorous acid solutions were prepared and standardized as described elsewhere.[2] All other chemicals were reagent grade.

Procedure.—Acidified (HCl or $HClO_4$), standard solutions of the complexes were prepared, and their absorption spectra were recorded. The oxidant was then added, Cl_2 as a gas and HOCl in solution. Visual observation indicated that, under the experimental conditions used, the reactions proceeded to completion within 1 min. However, in most instances the solutions were allowed to stand for 5 min. (Cl_2 experiments) or 15 min. (HOCl experiments). For the experiments with Cl_2, the excess oxidant was removed by a stream of nitrogen. For the experiments with HOCl, the excess oxidant was reduced with NaBr or NaCl, and the Br_2 or Cl_2 formed was removed by a stream of nitrogen.

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