in the *o*-phenylenebis(dimethylarsine) complexes. The four broad absorption bands between 6 and 30 kK are electronic transitions of the complex. A detailed examination of the electronic spectra of these iron nitrosyl complexes will be presented in a subsequent paper.

Acknowledgments.—The authors are indebted to Professor M. Wacks for the analysis of oxygen in these complexes by neutron activation. The authors gratefully acknowledge the National Science Foundation (Grant GP-5752) for support of this work.

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The Electronic Absorption Spectrum and Bonding in the $Cu_2Cl_6^{2-}$ Dimer

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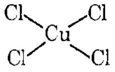
Received October 8, 1966

The electronic absorption spectra of several red copper(II) chloride compounds containing planar $Cu_2Cl_6^{2-}$ dimers have been measured. In addition to the normal charge-transfer and d–d transitions typical of square-planar $CuCl_4^{2-}$ ions, a new band, characteristic of the dimeric species, is present at 19,000 cm^{-1}. This band is polarized parallel to the Cu–Cu direction of the dimer. A molecular orbital description of the bonding in the dimer is presented and the origin of the anomalous 19,000-cm^{-1} band is explained.

Introduction

Recent investigations into the structural and spectral properties of copper(II) chloride complexes have revealed several heretofore unknown geometrical configurations.[1–9] Among those of particular interest have been the square-planar $CuCl_4^{2-}$ ion[4–6,8] (I) and the planar $Cu_2Cl_6^{2-}$ dimer[1–3] (II) The first of these has provided the opportunity to study in detail the properties of a simple square-planar species and contrast them with the properties of the more thoroughly studied distorted tetrahedral $CuCl_4^{2-}$ ion.[10–16] The second species is of interest because of the unusual optical[2,3] and magnetic properties[2,17–19] involved in the dimeric nature of the complexes. Since the $Cu_2Cl_6^{2-}$ dimer can be simply visualized as being formed by the union of two $CuCl_4^{2-}$ ions by the sharing of a pair of bridging chlorines, it makes it possible to correlate the properties of the dimer with the simpler monomer and sort out the features which are uniquely characteristic of the dimer. This article will report on an investigation of the electronic absorption spectrum of the $Cu_2Cl_6^{2-}$ dimer and an interpretation of its properties in terms of a simple molecular orbital correlation diagram.



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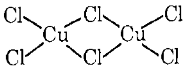

II

The compounds studied included $LiCuCl_3 \cdot 2H_2O$,[1] $KCuCl_3$,[2] $(CH_3)_2NH_2CuCl_3$,[3,20] and $(CH_3)_2CHNH_3CuCl_3$.[20] All four compounds are a deep garnet red and, when examined with polarized light, show strong yellow-red or green-red pleochroism.[3] For the case of the first three compounds, where the structure is known, it has been shown that compounds appear red when the electric vector of the polarized light is nearly parallel to the Cu–Cu direction.

Experimental Section

All compounds were prepared as described in previous work.[1–3,20] For each compound, except $KCuCl_3$, it was possible to obtain quite large crystals by slow evaporation of water or ethanol (or mixtures of the two) solutions in a desiccator with the use of a suitable desiccant. Thin single crystals for spectra work were ground or etched with an appropriate solvent. It was not always possible to obtain crystals thin enough for investigation of the visible and ultraviolet regions owing to the larger extinction coefficients for bands in this area. For these compounds, the spectra were obtained by the use of mineral oil and/or hexachlorobutadiene mulls. Since no isomorphous compounds exist, it was not possible to use a diluent technique. All spectra were recorded using a Cary Model 14 spectrophotometer. The results are summarized in Table I. For comparison purposes, the bands present in a typical square-planar complex, $(C_2H_5NH_3)_2CuCl_4$, are also given.

The polarization properties of the 19,000-cm^{-1} band were investigated using a polarizing microscope. The necessary

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TABLE I

SUMMARY OF SPECTRAL DATA[a] (IN CM^{-1})

Type of transition	$KCuCl_3$	$LiCuCl_3 \cdot 2H_2O$	$(CH_3)_2NH_2CuCl_3$	$(CH_3)_2CHNH_3CuCl_3$	$(C_2H_5NH_3)_2CuCl_4$[b]
Charge transfer					
σ	49,000 sm	49,000 sm	49,000 sm	~48,000	49,000 sm
	44,500 sh	44,000 sh	44,500 sh	44,500 sh	38,500 b, sh
π (bonding)	31,000 b	37,000 b	37,000 b	~34,000	33,000 b
π(nonbonding)	22,700 sm	24,000 sm	22,700 sm	25,000 sm	24,000 sm
π dimer	19,200 sm	19,600 sm	18,800 sm	18,500 sm	. . .
d–d transitions	12,900 b	12,500 b	12,900 b	12,500 b	12,800 b
	10,500 sh		10,800 sh	11,500 sh	10,500 sh

[a] The following notations are used: sm, sharp maxima; sh, shoulder; b, broad band. [b] Data for the square-planar $CuCl_4^{2-}$ ion. Obtained from ref 6.

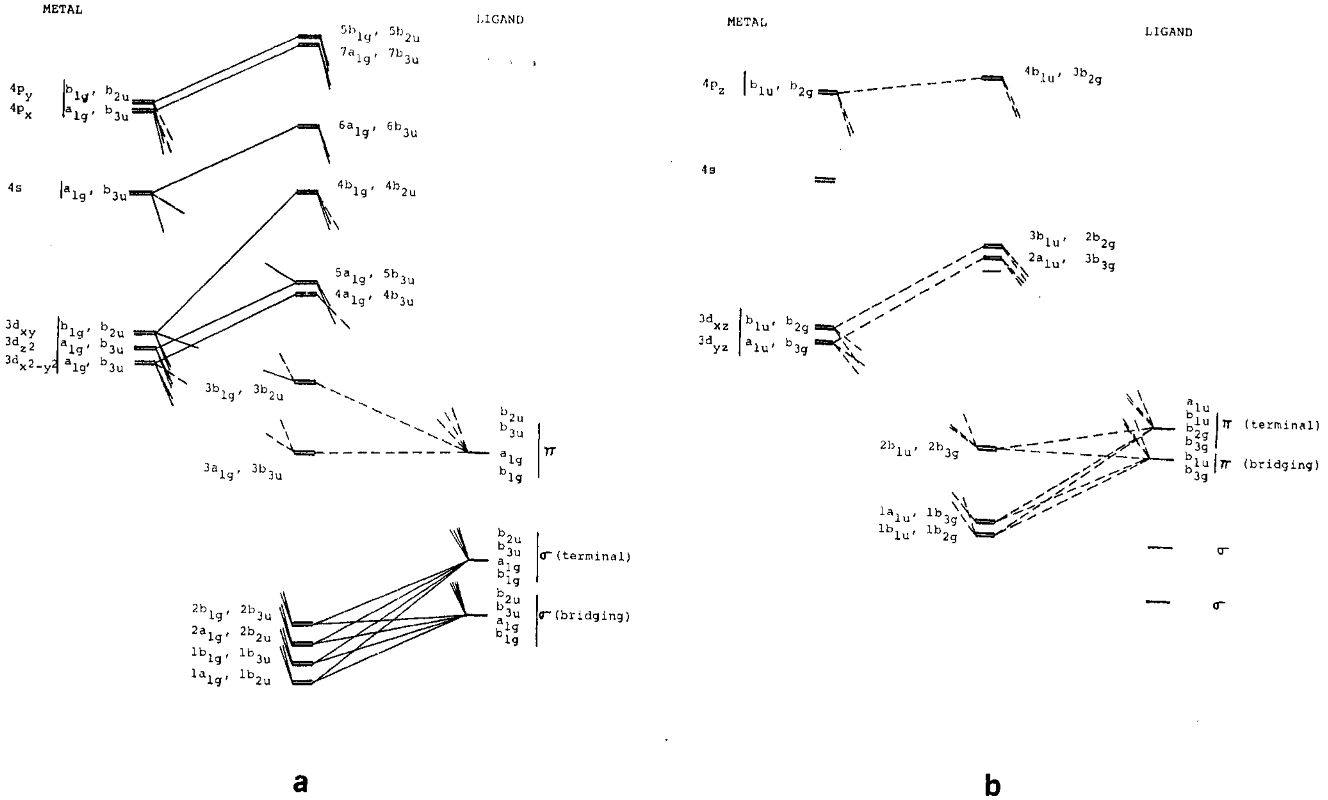

Figure 1.—(a) In-plane bonding in the $Cu_2Cl_6^{2-}$ dimer; (b) out-of-plane bonding in the $Cu_2Cl_6^{2-}$ dimer.

wavelength region was selected through the use of appropriate filters and the intensity of the transmitted radiation was measured with a Photovolt Series 520 photometer. In this manner, a plot of the intensity of the transmitted light *vs.* crystal orientation could be obtained, and, thence, from a study of the crystal morphology, the direction of the polarization of the band with respect to the crystal axes could be obtained. The results are summarized in Table II.

TABLE II

POLARIZATION PROPERTIES OF THE 19,000-CM^{-1} BAND

Compound	Lattice direction of maximum absorption	Lattice direction nearest projection of Cu–Cu direction
$KCuCl_3$	[201]	[201]
$LiCuCl_3 \cdot 2H_2O$	[201]	[201]
$(CH_3)_2NH_2CuCl_3$	[301]	[301]

Discussion of Spectra

As exemplified by the data in Table I, there is considerable similarity between the spectra obtained for the $Cu_2Cl_6^{2-}$ dimers and that found for the square-planar $CuCl_4^{2-}$ ion. With the exception of the band at 19,000 cm^{-1} very little difference is noted. Hence the interpretation of these bands can be made on the basis of the spectral assignments made for the square-planar $CuCl_4^{2-}$ ion.[6] The molecular orbital correlation diagram for this species is shown in Figure 1. All three of the expected d–d transitions are located under the envelope of the band whose maximum is in the 12,800–13,000-cm^{-1} region. The three main charge-transfer bands are assumed to be due to transitions arising from the π-nonbonding (24,000-cm^{-1}), π-bonding (33,300-cm^{-1}), and σ (49,000-cm^{-1}) orbitals. These same assignments will be carried over to the dimer and the observed bands, with the exception of the 19,000-cm^{-1} band, will arise from transitions starting from the same general type of orbitals as in the monomer.

Since the position of the d–d band does not change in going from the square-planar monomeric species to the dimer, there is no strong perturbation of the electronic environment involved in the formation of the dimer. In fact, on account of the large Cu–Cu distance of 3.44 A,[2] no direct metal–metal interaction is anticipated. This is in sharp contrast to the much studied copper(II) acetate dimer[21–24] where a direct interaction has not been eliminated and it is not possible to study the electronic structure of monomer species directly. Thus the $Cu_2Cl_6^{2-}$ ion truly presents a valuable opportunity to decipher the electronic structure of a dimeric species.

The polarization of the 5300-A band was studied for the compounds $LiCuCl_3 \cdot 2H_2O$, $KCuCl_3$, and $(CH_3)_2NH_2CuCl_3$. In each case a thin crystal which completely covered the field of the microscope was mounted so that the *b* axes of the monoclinic crystals were parallel to the path of the light. This orientation was chosen since the Cu–Cu vectors of all dimers are oriented in the same direction when projected onto the *ac* plane. In each case it was found that the maximum absorption was parallel to a particular lattice direction of the type [*u*0*w*].[25] That the maximum absorption must necessarily be parallel to a lattice direction can be shown from exciton theory.[26] The minimum absorbance was perpendicular to this direction but still in the *ac* plane. In each case, the direction of maximum absorption was parallel to the lattice vector nearest the projection of Cu–Cu vector in the dimer onto the *ac* plane. For example, in $KCuCl_3$, the maximum absorption occurs when the electric vector of the polarized light is parallel to the [201] direction while the projection of the Cu–Cu vector onto the *ac* plane makes an angle of approximately 4° with the [201] direction. Since the difference between the projection of the Cu–Cu direction and the direction of maximum absorption is less than 6° in all cases, it can safely be assumed that for a free dimer, the direction of maximum absorption would be parallel to the Cu–Cu direction. Thus the 19,000-cm^{-1} band is strongly polarized along the Cu–Cu direction despite the fact, as shown previously, that no direct metal–metal interaction exists. The origin of this anomalous band will be investigated in the following section.

Molecular Orbital Treatment

A molecular orbital correlation diagram for the $Cu_2Cl_6^{2-}$ dimer can be constructed in the normal manner. The complex has D_{2h} symmetry and symmetry orbitals can be obtained by group theoretical means from the appropriate valence orbitals on the metals or ligands. The 3d, 4s, and 4p orbitals on the metal and $3p\sigma$ and $3p\pi$ orbitals on the ligands will be used as the basis set.[27]

The energy level diagram for the in-plane σ and π orbitals of the planar $Cu_2Cl_6^{2-}$ ion is given in Figure 1a and for the out-of-plane π orbitals in Figure 1b. The metal symmetry orbitals are shown in the left-hand column, the ligand symmetry orbitals in the right-hand column, and the molecular orbitals in the central column. The metal symmetry orbitals come in degenerate pairs since they are formed from two atomic orbitals, one from each of the noninteracting metal atoms. Thus there is no difference in energy between the symmetric and antisymmetric combinations. For the in-plane ligand orbitals each bridging chlorine contributes a pair of σ-bonding orbitals while each terminal chlorine contributes a σ orbital and a π orbital, giving a total of 12 symmetry orbitals. In Figure 1a, these are grouped together according to the above classification. A comparison of the in-plane bonding for the dimer with the square-planar ion reveals that the number of orbitals doubles with the exception of the π orbitals. Hence the σ-bonding system remains unchanged in going from the monomer to the dimer but the π system will be altered. The four dimer in-plane π SO groups have symmetries a_{1g}, b_{1g}, b_{2g}, and b_{3u}. The assignment of their positions in the energy level scheme for the dimeric ion is difficult to predict although they must lie in the same general region as the bonding and nonbonding in-plane π MO groups of the monomer. These positions will be assigned by analyzing the polarization properties of the absorption spectrum.

A similar examination of the out-of-plane π orbitals can be made. Again there are twice as many metal SO groups in the dimer as in $CuCl_4^{2-}$, but the number of ligand SO groups only increases from four to six. The six SO groups of the dimer correspond to the bonding π orbitals of the monomer but there is no analog to the nonbonding orbital of the monomer. Thus the energy level scheme obtained for the out-of-plane π system is identical with that for the square-planar $CuCl_4^{2-}$ except that the ligand nonbonding orbital is missing.

The valence electrons from the chlorines can be accommodated in the in-plane MO groups up through $3b_{1g}$ and $3b_{2u}$ and the out-of-plane orbitals up through $2b_{1g}$ and $2b_{3g}$. Sixteen of the valence electrons from the copper(II) ions (18 all together) occupy, in order of increasing energy, the in-plane orbital $4a_{1g}$, $4b_{3u}$, $5a_{1g}$, and $5b_{3u}$ and the out-of-plane π orbitals $2a_{1u}$, $3b_{3g}$, $3b_{1u}$, and $2b_{2g}$. The remaining pair will be distributed between the $4b_{2u}$ and $4b_{1g}$ orbitals in some manner, depending on the nature of the ground state. It is shown in another paper[19] that the ground state is a singlet with a triplet state lying about 40 cm^{-1} above the ground state. Since these two orbitals are nearly degenerate, the triplet state will certainly be appreciably populated at room temperature. In the following discussion of the polarization of the allowed transitions, it will be assumed that the observed transitions are both singlet–singlet and triplet–triplet transitions, *e.g.*, that the transitions arise from either the $^1B_{3u}$ state or the $^3B_{3u}$ state.

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In Table III, the polarizations of the various allowed transitions are summarized. The x axis is defined as parallel to the Cu–Cu direction, the y axis as perpendicular to the Cu–Cu direction and in the plane of the dimer, and the z axis as perpendicular to the plane of the dimer. Thus the transitions which comprise the 19,000-cm^{-1} band must originate from molecular orbitals of b_{1g} and b_{2u} symmetry. Since the energy of transition is close to that of the first charge-transfer band of the monomer, the appropriate orbitals must be the $3b_{1g}$ and $3b_{2u}$ which arise primarily from the in-plane π-bonding levels. Hence, these orbitals can be placed some 19,000 cm^{-1} in energy below the highest d orbitals.

TABLE III

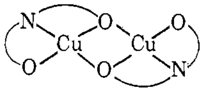
POLARIZATION OF ALLOWED TRANSITIONS

Types of transition	Polarization
$nb_{1g} \rightarrow 4b_{2u}$	x
$nb_{2u} \rightarrow 4b_{1g}$	x
$na_{1g} \rightarrow 4b_{2u}$	y
$nb_{3u} \rightarrow 4b_{1g}$	y
$nb_{3g} \rightarrow 4b_{2u}$	z
$na_{1u} \rightarrow 4b_{1g}$	z

Discussion

Magnetic Properties.—The molecular orbital scheme proposed in this paper favors a ground state of B_{3u} symmetry in which both the $4b_{1g}$ and $4b_{2u}$ orbitals are singly occupied. Recent neutron diffraction[18] and magnetic susceptibility studies[19] have indicated that the ground state is the singlet state. This is in accord with results of studies on several other bibridged copper(II) complexes,[28–31] primarily with the oxygen-bridged type. It is clear that the magnetic interaction almost certainly proceeds *via* an indirect spin–spin coupling and not *via* a direct metal–metal interaction. Recent calculations by Schlueter, *et al.*,[32] indicate that with a Cu–Cu distance of 3.06 A the overlap integral is less than 10^{-5}. The g values obtained by esr experiments for the $Cu_2Cl_6^{2-}$ dimer[33] are quite similar to those for the square-planar $CuCl_4^{2-}$ ion. Thus the amount of spin delocalization must be comparable, allowing for sufficient spin density at the bridging chlorines for interactions of the type needed to occur.

Hatfield and Bunger have discussed the magnetic interactions in Schiff base complexes in which the dimeric unit involves bridging oxygen atoms (III).


III

These dimers have a ground-state singlet approximately 250 cm^{-1} below the triplet state. Hatfield has proposed a molecular orbital interpretation of the singlet–triplet transition involving the out-of-plane π bonding in the $\mathrm{Cu}{<}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\,}}{>}\mathrm{Cu}$ bridging unit. They conclude that the singlet–triplet separation is dependent upon the strength of the out-of-plane π bonding. This is in direct contradiction to the results presented in the previous section of this paper. Unfortunately, they neglected to allow for occupancy of the antibonding σ orbitals in their molecular orbital treatment. Hence they assumed high-energy π orbitals (primarily 4p of the copper atoms) were occupied while lower energy σ orbitals ($3d_{xy}$ and 4s of the copper atom) were empty.

Spectra.—A polarized absorption band corresponding to the 5300-A band in the $Cu_2Cl_6^{2-}$ dimer has been observed in other bibridged copper(II) dimers.[34] The existence of this band in the visible region is apparently a general phenomenon and can be used as a criterion for identifying dimeric copper(II) species. The polarization of this band has served as a useful tool in this laboratory both as an aid in identifying dimers and also as an aid in the solution of crystal structure problems since the direction of polarization automatically gives the orientation of the Cu–Cu direction in the dimer.

In general, then, it will be expected that the electronic absorption spectrum of a planar bibridged copper(II) dimer will be essentially the same as that of the corresponding monomer with the exception of a new band which will arise owing to a change in the nature of the in-plane π-bonding orbitals. There is no significant change in the nature of the σ-bonding system, as evidenced by the constancy of the d–d transitions and of the third charge-transfer band. Thus the spectral properties of this system can be understood in terms of a simple molecular orbital treatment based on the assumption that the electronic structure of the square-planar $CuCl_4^{2-}$ ion is only slightly perturbed by the dimer formation.

Acknowledgment.—This work was supported by the Washington State University Research Committee and by Petroleum Research Fund Grant No. 1592-A3.

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