of fluorine ligands. Partial double bonding, which can be invoked for the NF molecule

$$:\!\mathrm{N{-}F}\!: \longleftrightarrow \,:\!\mathrm{N{=}F}$$

(r = 1.3173 Å),[18] is unlikely for NF_4^+ because all of its atoms already possess an electron octet.

The problems previously encountered with solving a crystal structure of an NF_4^+ salt appear to be largely due to ion rotation and/or disorder in these salts. The main difficulty consisted of finding a static model with nonrotating ions that could describe a dynamic structure with rotating ions. The thermal parameters of the atoms from the X-ray data and vibrational spectroscopy coupled with a group factor analysis were found to be very useful for the detection and understanding of ion rotation. In the case of ion rotation, the X-ray analysis can result in an apparent lowering of the symmetry and in a nonequivalence of ions, which have no real physical meaning. Similarly, partial structure solutions or solutions in which the geometry of one set of ions has to be constrained can result in unreliable bond lengths with deceptively small estimated standard errors.

Acknowledgment. The work at Rocketdyne was sponsored by the Office of Naval Research and the U.S. Army Research Office. We thank Dr. M. Watkins and J. A. Feng for assistance during the structural analysis of $NF_4Sb_2F_{11}$ and Dr. P. Charpin for helpful comments.

Registry No. NF_4BF_4, 15640-93-4; NF_4SbF_6, 16871-76-4; $NF_4Sb_2F_{11}$, 58702-89-9.

Supplementary Material Available: A table of anisotropic thermal parameters for NF_4BF_4 (1 page); a listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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Structural and Magnetic Properties of Dimorpholinium Hexahalodicuprate(II) Salts: Study of Two Planar $Cu_2X_6^{2-}$ Dimers

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Received January 6, 1988

The chloride and bromide analogues of the title compound were synthesized, and the X-ray crystal structure of the former compound was determined. Magnetic susceptibility and EPR studies were carried out on both compounds. The crystal structure of the chloride salt yielded a triclinic structure, space group $P\bar{1}$, with a = 7.414 (2) Å, b = 8.686 (2) Å, c = 14.766 (4) Å, α = 79.16 (2)°, β = 82.20 (2)°, γ = 74.19 (2)°, Z = 2, d_{calcd} = 1.94 g/cm^3, and R = 0.0527. The structure consists of isolated planar dimers with each copper atom semicoordinated to two oxygen atoms in what may be described, on the average, as a 4+2 elongated octahedral geometry. The magnetic exchange interaction in the two compounds is predominantly antiferromagnetic with a singlet–triplet splitting energy of J/k = −43.5 (1) K for the chloride and J/k = −131 (2) K for the bromide. EPR and magnetic studies on both compounds indicate that magnetically these compounds are not isolated dimers. EPR studies supplement both the structural and magnetic studies.

Introduction

There have been numerous copper(II) halide dimers of $Cu_2X_6^{2-}$ stoichiometry studied in the last several years,[1,2] but only recently have isolated planar dimers been discovered.[3] The copper(II) halide dimers studied to date belong to one of the following geometries: planar, bifolded, or twisted.[4] The bifold distortion, which is symbolized by σ, involves the angle between the central Cu_2X_2 plane and the terminal CuX_3 planes,[5] while the twist distortion, denoted by τ, refers to the angle between the bridging Cu_2X_2 plane and the terminal CuX_2 planes.[4] The planar dimers normally form stacks with the Cu(II) ions in sites of 4+2 coordination geometry, while the bifolded dimers form stacks with the Cu(II) ions in 4+1 coordination geometry. The twisted dimers are isolated species in which the Cu^{2+} ions in the $Cu_2X_6^{2-}$ units distort toward tetrahedral geometry in order to lower the chlorine–chlorine repulsion energy. The cations in these cases are large and do not hydrogen bond to the halide atoms in the dimer. Recently Tanaka discovered a planar isolated dimer with only a very small twist distortion,[3] in which the planar geometry is stabilized by interaction with dibenzotetrathiafulvalenium (abbreviated DBTTF) counterions. The morpholinium salts presented here are the second example of isolated planar dimers, in this case with the planar configuration stabilized by interaction with the organic cations.

Hatfield, while studying a series of planar dihydroxo-bridged Cu(II) dimers,[2] discovered the relationship between the bridging angle, ϕ, and the magnetic properties of these compounds; the antiferromagnetic coupling increases with increasing bridging angle. It is the purpose of magneto–structural studies to elucidate such correlations between not only the strength but also the anisotropy of the magnetic interactions and the geometrical and electronic structure of materials. Such relationships hold very well for the copper(II) halide dimers. Studies have shown that for bifolded chloride dimers, with $\phi \approx 95.5°$, J is antiferromagnetic for small values of σ and becomes ferromagnetic for $\sigma \geq 25°$.[6]

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0020-1669/88/1327-2454$01.50/0

Table I. X-ray Data Collection Parameters

compd name	dimorpholinium hexachlorodicuprate(II)
empirical formula	$C_8H_{20}N_2O_2Cu_2Cl_6$
mol wt	516.06
diffractometer syst	Siemens AED
cryst class	triclinic
space group	$P\bar{1}$
systematic absences	none
lattice constants^a	$a = 7.414$ (2) Å $b = 8.686$ (2) Å $c = 14.766$ (4) Å $\alpha = 79.16$ (2)° $\beta = 82.20$ (2)° $\gamma = 74.19$ (2)° $V = 447.5$ Å^3
$F(000)$	516
radiation	Mo Kα
cryst size	0.33 × 0.65 × 0.51 mm
abs coeff	33.3
calcd density	$\rho = 1.92$ ($Z = 2$)
type of abs cor	none
temp	25 °C
data collcn technique	ω scan
scan range	1.2
scan speed	3°/min (min), 12°/min (max)
check rflns	−2,3,2, monitored every 100 rflns
total no. of rflns	1462
2θ(max)	48
no. of unique rflns	983 (907 with $F > 3\sigma(F)$)
R for equiv rflns	0.0136
h,k,l range	$-8 < h < 8$, $-8 < k < 8$, $0 < l < 9$
structure soln package	Nicolet SHELXTL
structure soln technique	Patterson
$R = \sum\|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.0527
$R_w = [\sum w(\|F_o\| - [F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.0562
$w = 0.9212/[\sigma^2(F) + g(F)^2]$	$g = 0.003\,49$
function minimized	$\sum w(\|F_o\| - \|F_c\|)^2$
$\|\Delta/\sigma\|$(max)	0.28
total no. of params refined	166
thermal params	anisotropic on all non-H atoms
H atoms	constrained to C–H and N–H = 0.96 Å, thermal params fixed at 0.1
largest peak on final diff map	0.28 e/Å^3
most negative peak on final diff map	0.45 e/Å^3
extinction cor	none

^{a}Based on 25 reflections in the range 24° < 2θ < 28°.

It has also been observed that, for the twisted dimer, the exchange coupling is antiferromagnetic for $\tau = 0°$, becomes ferromagnetic for $\tau \approx 50°$, and becomes antiferromagnetic again for $\tau \approx 85°$.[7] In this paper magnetic susceptibility, EPR, and structural results are reported for two new isolated planar dimers: $(morphH)_2Cu_2Cl_6$ and $(morphH)_2Cu_2Br_6$ (morphH = morpholinium). Their properties are compared with those of other planar dimers.

Experimental Section

The compounds were prepared by combining equimolar mixtures of morpholine and $CuCl_2{\cdot}2H_2O$ ($CuBr_2$) in HCl (HBr) solution followed by concentrating the solution by evaporation. Crystals were grown by slow evaporation of dilute acid or alcoholic solution.[8]

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Dimorpholinium Hexachlorodicuprate(II)

atom	x/a	y/b	z/c	$U_{eq}{}^a$
Cu	1637 (2)	1619 (1)	1628 (1)	40 (1)
Cl(1)	4620 (3)	1965 (3)	3409 (3)	36 (1)
Cl(2)	1417 (3)	−1072 (3)	282 (3)	44 (1)
Cl(3)	1620 (3)	4235 (3)	2821 (3)	34 (1)
N	−3493 (10)	−3443 (9)	3422 (8)	32 (4)
O	−74 (16)	−171 (15)	3650 (14)	39 (6)
C(1)	−1942 (26)	−78 (23)	3810 (27)	46 (11)
C(2)	−3986 (18)	−1968 (15)	2600 (15)	78 (7)
C(3)	−1787 (15)	−3739 (15)	3059 (13)	69 (7)
C(4)	204 (23)	−1802 (23)	4166 (22)	39 (9)
C(1A)	−5096 (31)	−3115 (32)	671 (21)	55 (12)
C(4A)	−2940 (30)	−4827 (26)	1095 (18)	42 (10)
O(1)	−3730 (17)	−3671 (16)	81 (12)	39 (6)

^{a}The equivalent isotropic U is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Crystals of the two compounds grow as extremely fragile platelets that bend upon even the softest touch. As a consequence, crystals of quality suitable for X-ray structure analysis are extremely hard to obtain. In fact, none were ever found for the bromide salt. The optical properties of the crystals are most unusual, with both compounds exhibiting a very striking pleochroism. For the chloride salt, individual crystals appear milky gray or red with unpolarized light, depending on the orientation of the crystal with respect to the light source. However, with polarized light the crystals alternate between colorless and intense red-violet. The direction of intense absorption is approximately parallel to the Cu–Cu direction in the dimers. In unpolarized light, the transmitted light is also intensely red-violet when two crystals are superimposed with the polarization axes oriented at right angles to each other. Similar properties are observed for crystals of the bromide.

The crystal structure of the chloride salt was determined at Washington State University at room temperature on a Nicolet R3m/E system with Mo Kα radiation ($\lambda = 0.710\,69$ Å) and graphite monochromator.[9] The orientation matrix and lattice parameters of this triclinic crystal were optimized from the least-squares refinement to the angular settings of 25 carefully centered reflections with high Bragg angles. The SHELXTL 5.1 software package was used for data reduction and refinement.[10] These results were used in Parma to refine a data set taken on a larger crystal, and the results reported in this paper are from the refinement of that second data set. The data collection parameters are listed in Table I. Eleven reflections were omitted from the refinement because of counting errors.

Liquid-nitrogen-temperature susceptibility measurements on the bromide salt were taken at Washington State University on a PAR vibrating-sample magnetometer,[11] and the liquid-helium-range data were taken at Clark University on a similar apparatus. The chloride susceptibility data were collected at Washington State University.

The EPR powder spectra on both salts were taken on a Varian E-3 spectrometer at both room and liquid-nitrogen temperatures at Washington State University.

Results

Chloride Structure. The coordinates of the copper and chloride atoms were found by Patterson methods, and the positions of the carbon, nitrogen, and oxygen atoms were located from subsequent difference Fourier maps. The morpholinium cation appeared to be disordered. Half of the disordered atoms (O, C(1), and C(4)) appeared in two locations and thus were assigned site occupancy factors of $^1/_2$. Separate positions could not be identified for N, C(2), and C(3), but the thermal ellipsoids clearly indicated that disorder is present for C(2) and C(3). Several cycles of least-squares refinement of positional and isotropic thermal parameters were performed. Final refinement included variation of all positional parameters and anisotropic thermal parameters on the

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Table III. Selected Bond Angles (deg) and Bond Distances (Å) for Dimorpholinium Hexachlorodicuprate(II)

Bond Distances			
Cu-Cl(1)	2.249 (4)	O-C(1)	1.45 (3)
Cu-Cl(2′)	2.291 (4)	C(1)-C(2)	1.72 (2)
Cu-Cl(2)	2.275 (3)	C(2)-N	1.48 (2)
Cu-Cl(3)	2.240 (3)	N-C(3)	1.47 (2)
Cu-O	2.627 (1)	C(3)-C(4A)	1.70 (2)
C(4)-O	1.42 (2)	O(1)-C(1A)	1.43 (3)
C(4)-C(3)	1.70 (2)	O(1)-C(4A)	1.44 (2)
Bond Angles			
Cl(3)-Cu-O	88.4 (3)	O-C(4)-O(3)	110 (1)
Cl(2)-Cu-O	91.6 (3)	Cu-O-C(4)	123 (1)
Cl(2)-Cu-Cl(3)	175.6 (1)	C(4)-O-C(1)	112 (1)
Cl(2′)-Cu-O	92.9 (3)	Cu-O-C(1)	121 (1)
Cl(2′)-Cu-Cl(3)	91.5 (1)	O-C(1)-C(2)	109 (1)
Cl(2′)-Cu-Cl(2)	84.1 (1)	C(1)-C(2)-C(1A)	143 (1)
Cl(1)-Cu-O	87.2 (3)	C(1)-C(2)-N	98 (1)
Cl(1)-Cu-Cl(3)	92.6 (1)	N-C(2)-C(1A)	99 (1)
Cl(1)-Cu-Cl(2)	91.7 (1)	C(2)-N-O(3)	112 (1)
Cl(1)-Cu-Cl(2′)	175.9 (1)	C(4)-C(3)-N	101 (1)
Cu-Cl(2)-Cu(1)	95.8 (1)	N-C(3)-C(4A)	100 (1)

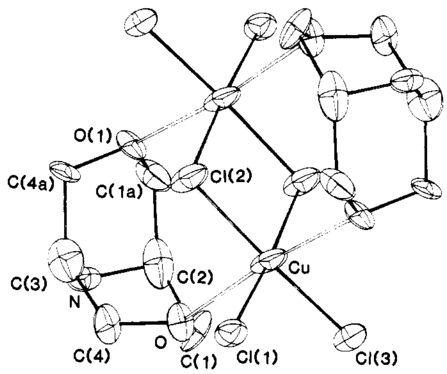

Figure 1. ORTEP diagram of (morphH)$_2$Cu$_2$Cl$_6$. The morpholinium cations are shown occupying two disordered sites.

Cu, Cl, C, N, and O atoms. The isotropic thermal parameters for the protons were set at 0.1. Final values of $R = 0.0516$ and $R_w = 0.0551$ were obtained for all reflections with $F \geq 3\sigma$ and $2\theta \leq 48°$. Positional parameters and equivalent isotropic thermal parameters are given in Table II, and selected bond angles and distances are shown in Table III.

Structure Description. The structure of the chloride salt revealed isolated planar dimers with each copper atom bonded to four chlorides in plane and semicoordinated to two of the disordered oxygen atoms out of plane in what may be described, on the average, as a 4+2 elongated octahedral geometry (Figure 1). The semicoordinated Cu–O distance is 2.607 (13) Å while the Cu–Cl terminal bond distances are 2.239 (4) and 2.240 (3) Å and the bridging Cu–Cl distances are 2.275 (3) and 2.291 (4) Å. Within the basal plane the trans Cl–Cu–Cl angles are 175.6 (1) and 175.9 (1)°. A least-squares plane was calculated for the Cu$_2$Cl$_6^{2-}$ unit, and the largest deviation from this plane was 0.004 Å. The morpholinium cations are disordered across a plane that contains the two bridging Cl atoms and is perpendicular to the Cu–Cu nuclear axis. This disorder explains how each copper atom appears semicoordinated, on the average, to two oxygen atoms when there are only two morpholinium molecules in the formula unit. The thermal ellipsoids of the Cu and Cl atoms are elongated in a direction perpendicular to the plane of the dimer. This elongation may be explained by assuming a 4+1 coordination of the copper atoms; at any given time, or orientation in the unit cell, the oxygen atom is coordinated either above or below the Cu atom. The bridging and bifold angles were found to be 95.8 and 0.0°, respectively. The crystal habit, morphology, and optical properties of the bromide are identical with those of the chloride; therefore, the two salts are believed to be isostructural.

Magnetics. The chloride and bromide salts show maxima in their powder susceptibilities at 53 and 145 K, respectively (Figures 2 and 3). At first inspection the structural data suggest that the data should be fit to the Bleaney–Bowers isolated dimer model,[18] but in actuality this model yielded no meaningful results. Examination of the structure revealed that the closest chlorine–chlorine contact between dimers was 3.942 Å (Figure 4). While this value is substantially greater than the sum of the van der Waals radii of the chloride ions (3.6 Å), this Cl–Cl contact does represent a possible exchange pathway, and thus the alternating-chain model was used to fit the data.[19] The Hamiltonian for this system reads as

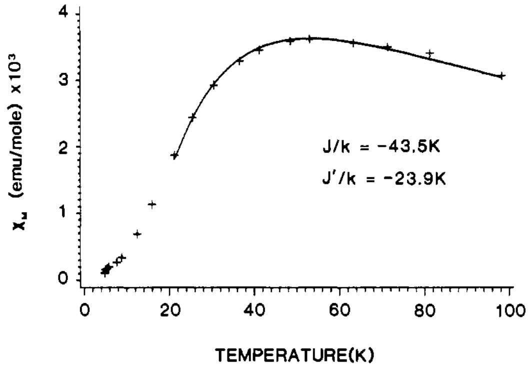

Figure 2. Plot of χ_m vs T for a powdered sample of (morphH)$_2$Cu$_2$Cl$_6$.

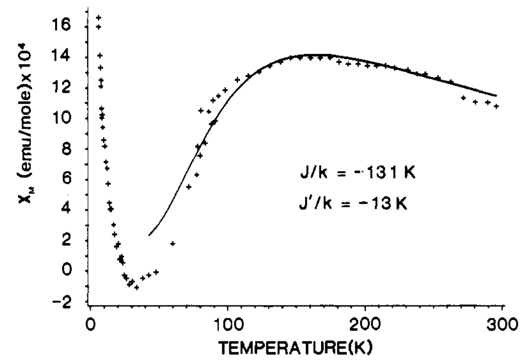

Figure 3. Plot of χ_m vs T for a powdered sample of (morphH)$_2$Cu$_2$Br$_6$.

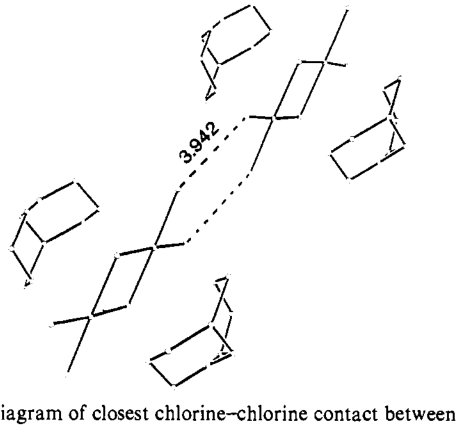

Figure 4. Diagram of closest chlorine–chlorine contact between dimers.

$$H = -2J \sum_{i=1}^{N/2} (S_{2i}S_{2i-1} + \alpha S_{2i}S_{2i+1})$$

The temperature at the maximum susceptibility uniquely defines the strongest antiferromagnetic coupling within the chain since the susceptibility of the alternating antiferromagnetic chain reaches a maximum at $T_{\max} \simeq 1.25(J/k)$, essentially independent of α. This fixes J/k at approximately −42 and −128 K for the chloride and bromide salts, respectively. The chloride salt data when fit

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Table IV. Structural and Magnetic Parameters of Planar $Cu_2X_6^{2-}$ Dimers

	X = Cl						X = Br				
cation	ϕ, deg	bridging dist, Å	σ, deg	J/k, K	$e_s - e_a$, eV	ref	ϕ, deg	bridging dist, Å	σ, deg	J/k, K	ref
K^+	96.0	2.314	4.5	−28	0.1153	23, 24	95.6	2.450	4.1	−95	23, 25
melaminium	95.8	2.334	7.6	−28	0.1140	17	95.6	2.468	7.5	−113	5
morpholinium	95.8	2.287	0	−44	0.1217					−131	
DBTTF[b]	96.2	2.284	0[a]	−67	0.1327	3	96.0	2.420	0	−127	3

[a] This work. [b] A slight twist distortion (τ = 6°) exists in this salt.

to the alternating-chain model, with g fixed at 2.20, yielded $J/k = -43.5$ (1) K and $J'/k = -23.9$ (1) K. The bromide salt data fit to the same model, with g fixed at 2.15, gave $J/k = -131$ (2) K, $J'/k = -13$ (2) K, and a 1.9 (3)% impurity. The impurity was taken into account by introducing the adjustable parameter Q, which multiplied the alternating-chain model as $1 - Q$. It is assumed that intradimer coupling may be ascribed to J and the interdimer coupling to J'.

EPR. The room-temperature EPR spectrum of the powdered crystals of the chloride salt consists of a broad symmetric line with peak-to-peak line width $\Delta H \approx 575$ G. Superimposed on this line is a narrower line with rhombic anisotropy. The powder spectrum at 77 K is nearly axial, but $g\|$ and $g\perp$ are not fully resolved. The apparent spectroscopic splitting factor (g) is 2.083 (3). The line width associated with the $g\perp$ feature is $\Delta H_\perp \approx 200$ G.

The powdered-crystal EPR spectrum of the bromide salt at room temperature consists of only a half-field line at a resonance field of 1818 G and a frequency of 9.118 GHz. At 77 K, the spectrum consists of an asymmetric line with $\Delta H \approx 200$ G and $g = 2.089$ (7) and a very broad line with $\Delta H \approx 4000$ G superimposed on the narrow asymmetric line.

Discussion

Spectroscopy. The structural results for $(morph)_2Cu_2Cl_6$ are consistent with the spectroscopic data previously reported.[11] The d–d transitions are centered at 12 500 cm^{-1} at room temperature. In the stacked planar dimers such as $KCuCl_3$ or $LiCuCl_3{\cdot}2H_2O$, this band is found at 12 500–12 900 cm^{-1}.[12] Thus, replacement of Cl^- in the semicoordinate position by O has little effect upon the room-temperature d–d spectra. Changes in energy levels certainly have occurred, but these are easily masked by the large bandwidths. It is to be noted that in the bifolded dimers, with $\sigma \geq 25°$, this band has shifted down into the 10 000–11 000-cm^{-1} range,[11,13,14] indicating that the folding of one of the trans Cl–Cu–Cl angles causes the d orbital energy levels to move closer together. Similarly, the tetrahedral distortion in the twisted dimers causes these bands to shift down to 9000–10 000 cm^{-1}.[15] In the far-IR spectrum, bands are observed at 313, 298, and 236 cm^{-1}, where the first band is usually associated with the terminal Cu–Cl stretch and the last two are associated with the bridging Cu–Cl stretches. These are at slightly higher frequencies than in the stacked dimers (NH_4CuCl_3, 311, 280, and 230 cm^{-1}, respectively;[16] $(melH_2)Cu_2Cl_6$, 300, 284, and 232 cm^{-1}, respectively;[17] indicating the Cu–Cl bonds are somewhat stronger (shorter) due to weaker axial interactions. These transitions appear to occur at lower energies in the bifolded dimers[8] due to the increased axial interactions ((pipH)$CuCl_3$, 287, 265, and 237 cm^{-1}; pipH = piperidinium) but at higher energies in the twisted dimers[15] (Ph_4XCuCl_3 (X = P, As, Sb), 325, 300, and 255 cm^{-1}) due to the shortening of the Cu–Cl bonds.

Magnetics. One of the goals of magneto–structural studies is to obtain correlations between structural and/or electronic properties of a system and the corresponding magnetic behavior. The results here are relevant to several such relationships that we have been investigating: the role of the ligand-to-metal charge-transfer energies upon the exchange coupling, the effect of distortion of the $Cu_2X_6^{2-}$ ion from planarity, and the consequences of interspecies halogen–halogen contacts.

Figure 5 shows a plot of magnetic exchange constants for a series of symmetrically bibridged copper(II) chloride salts vs those for bromide salts. It is seen that, for most of the ferromagnetic salts in the series, the magnitude of J/k is approximately the same irrespective of the halide ion. This trend changes as the salts become more antiferromagnetic; J/k decreases much more rapidly for the bromide salts than for the chloride salts. These differences may not be explained by structural arguments since little change in structure occurs between the chloride and bromide salts. However, if the factors influencing the contribution of the antiferromagnetic exchange to coupling are examined, an explanation is discovered.[20] In the Hoffmann[21] formalism, the exchange is expressed as

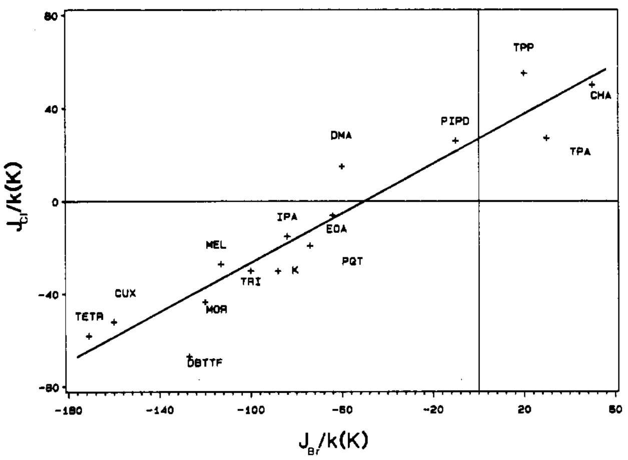

Figure 5. Plot of $[J/k]$(Cl) vs $[J/k]$(Br) for symmetric bibridged copper(II) halide salts.

$$2J = 2J_F - (\epsilon_s - \epsilon_a)^2/(J_{aa} - J_{ab})$$

Here J_{aa} and J_{ab} are one- and two-center Coulomb integrals, while ϵ_s and ϵ_a are the one-electron energies of the symmetric and antisymmetric combination of magnetic orbitals on the two metal centers. It may be seen from this equation that the antiferromagnetic contribution goes as $(\epsilon_s - \epsilon_a)^2$ and that the interaction becomes more ferromagnetic as ϵ_a approaches ϵ_s. Hay et al. argue that this antiferromagnetic term is inversely proportional to the difference in energies between the ligand orbitals and the magnetic orbital on the metal. This quantity may be estimated from the intense ligand-to-metal charge-transfer transitions, which occur at the UV–visible border line for the chloride salts (25 000–30 000 cm^{-1}) but are in the middle of the visible region for the bromide salts (15 000–20 000 cm^{-1}). It may be postulated from these data that the antiferromagnetic contribution to the exchange, J_{AF}, will be 2–3 times larger for the bromide than for the chloride salts. This is in excellent agreement with the experimental trends, as can be seen in Figure 5. A rough linear relationship, with a slope of approximately $^1/_2$, is readily observed.

It has also been demonstrated[5,22] that a general relationship exists between J and the bifold angle, σ, of the dimeric species, with a maximum antiferromagnetic coupling when $\sigma = 0°$ becoming ferromagnetic at $\sigma \approx 25°$ for the chloride salts and $\sigma \approx 35°$ for the bromide salts. On the other hand, for small values of σ ($\sigma < 10°$), J should be essentially independent of σ since the

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J vs σ curve must approach $J = 0$ with zero slope. Thus, for compounds in this region, any variations in J must be related to other structural parameters, such as the bridging angles, ϕ, and the Cu–X distances. When the data for the four sets of compounds with $\sigma < 10°$ listed in Table IV are examined, these influences can be seen and the variation in J/k values readily rationalized. For the potassium[23] and melaminium[17] salts, which exhibit a slight bifold distortion with long bridging Cu–Cl bonds, the antiferromagnetic exchange is relatively weak at $J/k = -28$ K.[17,24] In the morpholinium and DBTTF salts,[3] the bond distances are now much shorter and the exchange has become substantially more antiferromagnetic. The calculated values of $\epsilon_s - \epsilon_a$, for the chloride salts, based on the actual geometries, are also in good agreement with the observed J/k values. In particular, the strongly antiferromagnetic nature of the interaction in DBTTF is confirmed. Similar trends are seen for the bromide salts.[3,5,25]

It was mentioned earlier that the alternating-chain model was used to fit the susceptibility data of the morpholinium salts and that the isolated dimer yielded no meaningful results. This suggests that an interdimer exchange pathway exists, and this behavior may only be explained by the relatively short Cl···Cl contact (3.942 Å) discussed previously. Halide–halide contacts of this type play important roles in magnetic behavior in other compounds as well. A group of alkyldiammonium tetrachlorocuprate(II) salts form layered structures in which Cl···Cl contacts are exchange pathways for interlayer exchange. The chloride salts of $^+NH_3C_nNH_3^+$, where $n = 2$–5, have chlorine–chlorine distance/J' values of 3.649 Å/−13.7 K,[26] 4.548 Å/−1.7 K,[27] 4.941 Å/−0.16 K,[28] and 6.525 Å/−0.04 K,[27] respectively. A simple correlation between contact distance and the coupling constant, J', is observed. Other geometrical considerations, as well as inherent uncertainties in the measurement and calculation of J', must be taken into account as well, and this probably explains why the morpholinium contact distance of 3.942 Å corresponds to a rather large value of $J'/k \approx -22$ K. On the basis of this evidence the interdimer contacts in the morpholinium salts are responsible for the interdimer coupling. Thus, although isolated dimers exist structurally, magnetically there is strong interdimer coupling.

EPR. The EPR line widths of copper(II) halides are exchange-broadened due to phonon modulation of the exchange anisotropy, which leads to a linear temperature dependence proportional to $(\Delta g)^2 J^4$.[29,30] On the basis of the measured value of J and expected value of $\Delta g = g_\parallel - g_\perp$ for the copper(II) ion in the chloride salt, a line width of several hundred gauss is expected. Thus, the broad line at room temperature for the chloride salt is identified as the signal from the bulk sample. The narrower line then must be an impurity spectrum and has been identified as $CuCl_2 \cdot 2H_2O$. Similar impurity spectra (for $CuCl_2 \cdot 2H_2O$ powder with $g_1 = 2.25$, $g_2 = 2.19$, $g_3 = 2.05$[31,32]) have been observed for some other copper(II) chloride chains that were investigated at Washington State University. Due to the temperature dependence mentioned above, we expect, as observed, a narrower bulk line at liquid-nitrogen temperature. The temperature dependence of the line width also points to the fact that what we have is not a magnetically isolated dimer. Thus, as mentioned in the Magnetics part of Results, the closest Cl–Cl contact of 3.942 Å (Figure 4) between dimers is acting as a possible exchange pathway.

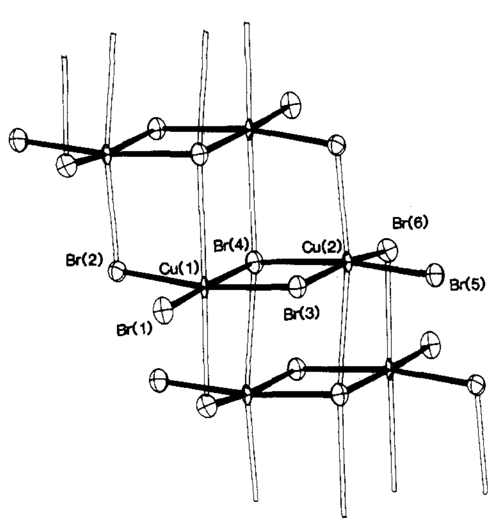

Figure 6. Illustration of $Cu_2Br_6^{2-}$ stacks in $(melH_2)Cu_2Br_6$.

The nearly axial spectrum at 77 K is consistent with a slightly elongated octahedral environment of the copper (II) ion. In our EPR studies on several antiferromagnetic copper(II) chloride dimer chains with organic cations, we found that, for smaller distortions ($\sigma \approx 0°$) and large antiferromagnetic interactions ($J/k \leq -20$ K), the line widths are so broad that $g_\parallel$ and $g_\perp$ are not resolved even at liquid-nitrogen temperature. Because of the J^4 dependence of ΔH upon J, we intuitively expect $g_\parallel$ and $g_\perp$ to be resolved only for bifold distortions in the range where the exchange coupling is small. We plan to put these observations together in a future publication.

In the case of the bromide salt, the existence of only a half-field line at room temperature is difficult to interpret. In low-dimensional magnetic systems, the long time tail of the correlation function hinders the collapse of the satellite lines into the main line and thus can make possible the observation of a half-field line,[33] but in the absence of EPR relaxation studies on this salt, such interpretation is only speculative.

Due to larger spin–orbit coupling and a stronger antiferromagnetic interaction, the EPR line widths of the copper(II) bromide salts are 10–20 times larger than those of the corresponding chloride salts.[34] Thus, the broad line at 77 K must be due to the exchange-coupled $Cu_2Br_6^{2-}$ chains. A completely unobservable line (too broad) at room temperature and a very broad line ($\Delta H \approx 4000$ G) at 77 K suggest the existence of exchange pathways between dimers as mentioned in the Magnetics part of the Discussion. The narrower line on which the broad line is superimposed at 77 K is attributed to an impurity in the sample. Again, such impurity spectra have been observed for some other bromide compounds that were studied at Washington State University, although the nature of the impurity has not been identified.

Conclusions

This study confirms that the magnetic properties of copper(II) halide salts are influenced greatly by the chemistry of the halide ion. The existence of lower lying charge-transfer states in the bromide salts enhances the antiferromagnetic contribution to the exchange as compared to that for the chloride salts. Thus, despite their similar structural characteristics, the magnetic behavior of copper(II) bromide and chloride salts is greatly modified by variations in the electronic structure of the halide ions. For the group of nearly planar copper(II) halide dimers, the exchange coupling is shown to be strongly influenced by the bridging Cu–X distances. This reinforces the idea that magneto-structural correlations in copper(II) halides are not a simple one-parameter

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Table V. Crystal Data for $(\mathrm{melH_2})\mathrm{Cu_2Br_6}$

empirical formula	$C_3H_8N_3Cu_2Br_6$
mol wt	734.65
diffractometer syst	Philips PW-1100
cryst class	monoclinic
space group	$P2_1/c$
lattice constants	$a = 7.03$ (2) Å $b = 10.477$ (3) Å $c = 19.769$ (7) Å $\beta = 95.76$ (1)° $V = 1448.7$ Å^3
$F(000)$	1344
radiation	Mo Kα
abs coeff	193.33 cm^{-1}
calcd density	3.367 g/cm^3 ($Z = 4$)
type of abs cor	North–Philips–Matthews technique
transmission (max, min)	0.996, 0.535
temp	22 °C
data collcn technique	ω–2θ
scan speed	2.4°/min
scan range	1.2°
no. of std rflns	2 (measd every 110)
total no. of rflns	2931
2θ range	5–50°
no. of unique rflns	1440 (1306 with $F > 3\sigma(F)$)
h,k,l range	$0 < h < 8$, $0 < k < 12$, $-23 < l < 23$
structure refinement package	SHELX-76
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\lvert F_o\rvert$	0.0533
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.0560
$w = 0.9871/[r^2(F) + g(F^2)]$	$g = 0.00259$
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
total no. of params refined	109
thermal params	anisotropic on Cu, Br; isotropic on C, N
largest peak on final diff map	1.4 e/Å^3
most negative peak on final diff map	−1.5 e/Å^3
extinction cor	none

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $(\mathrm{melH_2})\mathrm{Cu_2Br_6}$

atom	x/a	y/b	z/c	U_{eq}
Cu(1)	1744 (r)	573 (2)	896 (1)	10 (2)
Cu(2)	3358 (4)	1179 (2)	−755 (1)	10 (2)
Br(1)	1064 (3)	1958 (2)	1802 (1)	24 (1)
Br(2)	490 (3)	−1301 (2)	1403 (1)	20 (1)
Br(3)	2611 (3)	2458 (2)	217 (1)	18 (1)
Br(4)	2475 (3)	−655 (2)	−90 (1)	18 (1)
Br(5)	4561 (3)	3051 (2)	−1310 (1)	22 (1)
Br(6)	4419 (3)	−269 (2)	−1598 (1)	21 (1)
C(1)	1967 (31)	5806 (21)	−662 (9)	21 (5)
C(2)	324 (28)	4976 (19)	−1594 (8)	14 (4)
C(3)	3145 (33)	6181 (22)	−1727 (10)	26 (5)
N(1)	493 (22)	5126 (16)	−925 (7)	16 (4)
N(2)	1634 (23)	5469 (17)	−2009 (7)	16 (4)
N(3)	3294 (24)	6366 (16)	−1039 (7)	19 (4)
N(4)	2270 (26)	5983 (17)	26 (7)	22 (4)
N(5)	−1169 (24)	4422 (16)	−1911 (7)	16 (4)
N(6)	4369 (28)	6590 (19)	−2125 (8)	28 (4)

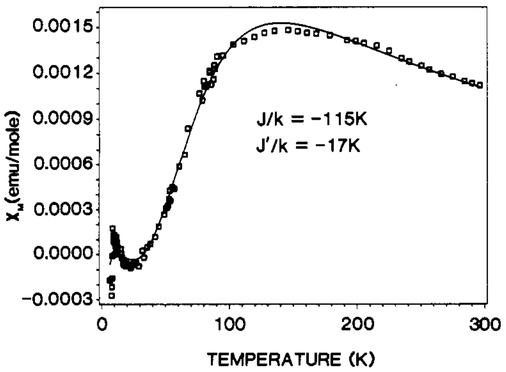


Figure 7. Plot of χ_m vs T for a powdered sample of $(\mathrm{melH_2})\mathrm{Cu_2Br_6}$.

Table VII. Bond Distances (Å) and Angles (deg) for the $\mathrm{Cu_2Br_6}^{2-}$ Stacks

	Bond Distances		
Cu(1)–Br(1)	2.390 (3)	Cu(2)–Br(3)	2.475 (3)
Cu(1)–Br(2)	2.411 (3)	Cu(2)–Br(4)	2.466 (3)
Cu(1)–Br(3)	2.498 (3)	Cu(2)–Br(5)	2.421 (3)
Cu(1)–Br(4)	2.433 (3)	Cu(2)–Br(6)	2.398 (3)
Cu(1)–Br(6′)	2.924 (4)	Cu(2)–Br(2)	2.864 (4)
Cu(1)–Br(4′)	3.224 (4)	Cu(2)–Br(4)	3.287 (4)
	Bond Angles		
Br(3)–Cu(1)–Br(4)	84.6 (1)	Br(5)–Cu(2)–Br(6)	94.0 (1)
Br(2)–Cu(1)–Br(4)	91.0 (1)	Br(4)–Cu(2)–Br(6)	89.6 (1)
Br(1)–Cu(1)–Br(4)	174.6 (1)	Br(3)–Cu(2)–Br(6)	170.3 (1)
Br(2)–Cu(1)–Br(3)	170.5 (1)	Br(4)–Cu(2)–Br(5)	171.7 (1)
Br(1)–Cu(1)–Br(3)	90.0 (1)	Br(3)–Cu(2)–Br(5)	91.1 (1)
Br(1)–Cu(1)–Br(2)	94.2 (1)	Br(3)–Cu(2)–Br(4)	84.3 (1)
Cu(1)–Br(3)–Cu(2)	94.6 (1)	Cu(1)–Br(4)–Cu(2)	96.5 (1)

problem but must be described in a multiparameter hyperspace.

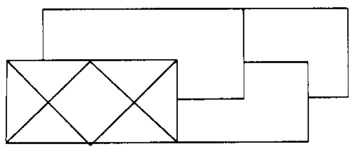
EPR and magnetic studies of both chloride and bromide compounds indicate the existence of exchange pathways between dimers. The short Cl–Cl link as revealed by a close examination of the crystal structure of the chloride salt is a possible exchange pathway. We believe a similar exchange pathway exists for the bromide compound also.

Acknowledgment. This work was supported by NSF Grants DMR 8219430 and INT 8219425. The Nicolet R3m/E facility at Washington State University was established through funds provided by NSF Grant CHE 8408407 and by The Boeing Co. The magnetic work done at Clark University was supported by NSF Grant DMR 8306432.

Appendix

As part of our study of the structural and magnetic correlations between the chloro and bromo complexes of copper(II), we have determined the crystal structure of $(\mathrm{melH_2})\mathrm{Cu_2Br_6}$, where $\mathrm{melH_2}$ is the dication of melamine, $C_3N_3(NH_2)_3$, 2,4,6-triamino-1,3,5-triazine. The magnetic properties have been reported in a previous paper.[5] The crystal structure is isomorphous with that of the corresponding chloride salt. Data collection parameters and refinement details are given in Table V, with final positional parameters and equivalent isotropic thermal parameters in Table VI and pertinent bond distances and angles for the $\mathrm{Cu_2Br_6}^{2-}$ species in Tables VII. Bond distances and angles for the melaminium ion show no unusual features. Initial positions were taken from the chloride structure. Hydrogen atoms were not included in the final refinement. The structure is illustrated in Figure 6.

The crystal structure is uneventful with respect to differences from the corresponding chloride structure. Each copper ion has an approximately planar primary coordination sphere with longer, but unequal, semicoordinate bonds to bromide ions in adjacent dimers. This gives the copper ions what may be called a 4+1+1 coordination geometry, and because of this, the dimers are slightly nonplanar. Specifically, the terminal bromide ions that are involved in semicoordinate bond formation tip toward the adjacent dimer so as to shorten that bond. The bridging bromide ions similarly involved do not do this. Of the two bridging bromide ions, only Br(4) is involved in semicoordinate bond formation. This causes the Cu(1)–Br(4)–Cu(2) intradimer bridging angle to be nearly 2° larger than its Cu(1)–Br(3)–Cu(2) counterpart. As is typical, the terminal Cu–Br bond lengths (2.405 Å, average) are substantially shorter than the bridging length (3.468 Å, average). Finally, the stacking arrangement (I) is the same as in the chloride structure.



I

The magnetic susceptibility data are reproduced in Figure 7, since they were not shown in ref 5, and give an intradimer exchange coupling of $J/k = -115$ (1) K and an effective interdimer coupling of $J'/k = -17$ (1) K with $g = 2.18$ and a 0.8% impurity.

Registry No. $(morphH)_2Cu_2Cl_6$, 61825-58-9; $(morphH)_2Cu_2Br_6$, 114694-36-9; $(melH_2)Cu_2Br_6$, 110132-63-3.

Supplementary Material Available: Table S1, listing anisotropic thermal parameters, Table S2, listing H atom coordinates and isotropic thermal parameters, and Table S3, listing bond distances and angles, torsion angles, least-squares planes, and interatomic contacts (7 pages); listings of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Studies on the α and β Isomers of Complexes of the Type $Re_2X_4(LL)_2$. Structural Characterization of α- and β-$Re_2Cl_4(dppee)_2$ (dppee = *cis*-$Ph_2PCH{=}CHPPh_2$)

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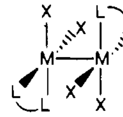
Received January 28, 1988

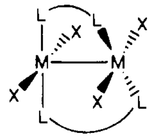
The first structural study on a pair of α and β isomers of dirhenium(II) of the type $Re_2X_4(LL)_2$ (X = Cl, Br; LL = bidentate phosphine ligand) has been carried out in the case of X = Cl and LL = *cis*-$Ph_2PCH{=}CHPPh_2$ (dppee). Crystals of α-$Re_2Cl_4(dppee)_2$·*n*-PrOH, which were grown from CH_2Cl_2/*n*-propyl alcohol, crystallize in the triclinic space group $P\bar{1}$ with the following unit cell dimensions: $a = 13.485$ (3) Å, $b = 17.556$ (5) Å, $c = 11.952$ (3) Å, $\alpha = 87.24$ (2)°, $\beta = 100.12$ (2)°, $\gamma = 110.66$ (2)°, $V = 2606$ (3) Å^3, and $Z = 4$. The structure was refined to $R = 0.037$ ($R_w = 0.048$), with quality of fit 1.403, for 5384 data with $F_o^2 > 3\sigma(F_o^2)$. There are two crystallographically independent molecules, which are essentially identical structurally with an average $Re\equiv Re$ distance of 2.258 Å. The centrosymmetric molecules contain chelating dppee ligands and possess an eclipsed rotational geometry. The isomer β-$Re_2Cl_4(dppee)_2$ crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 16.917$ (2) Å, $b = 12.992$ (4) Å, $c = 22.990$ (7) Å, $\beta = 106.86$ (2)°, $V = 4836$ (4) Å^3, and $Z = 4$. The structure was refined to residuals of $R = 0.088$ and $R_w = 0.074$ and quality of fit 2.389 for 3002 data with $F_o^2 > 3\sigma(F_o^2)$. Refinement of the structure was complicated by a disorder in which a second set of rhenium atoms (20% occupancy) was found, centered at the same point as the principal pair (80% occupancy), and with the Re–Re vector roughly perpendicular to that of the primary Re_2 unit. The $Re\equiv Re$ distance was refined to 2.242 (3) Å for the major component of the disorder. The molecules possess an overall staggered geometry in which the dppee ligands bridge the two metal centers. The resulting six-membered ring conformations in both the principal and minor molecules are of the type well-known for cyclohexene, namely, a flattened chair or half-chair. Synthetic procedures have been developed for the preparation of α-$Re_2X_4(dppe)_2$ (X = Cl, Br; dppe = $Ph_2PCH_2CH_2PPh_2$), complexes whose β isomers have been reported previously. The first successful chemical oxidation of α isomers of dirhenium(II) has been accomplished; α-$Re_2Cl_4(LL)_2$ complexes (LL = *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2P(CH_2)_3PPh_2$) have been oxidized by $(Cp_2Fe)PF_6$ in CH_2Cl_2 to give paramagnetic α-$[Re_2Cl_4(LL)_2]PF_6$.

Introduction

In a recent report we described the first instance of the isolation of dirhenium(II) complexes of the type $Re_2X_4(LL)_2$ (X = halogen; LL = bidentate phosphine ligand) in both their α and β isomeric forms (see I and II).[2] Both isomers were isolated in the case of $Re_2Br_4(depe)_2$ and $Re_2X_4(dppee)_2$ (X = Cl, Br; depe = $Et_2PCH_2CH_2PEt_2$; dppee = *cis*-$Ph_2PCH{=}CHPPh_2$), and details of the spectroscopic and electrochemical properties of these complexes were reported. Subsequently, we have succeeded in obtaining α- and β-$Re_2Cl_4(dppee)_2$ in a crystalline form suitable for X-ray structure determinations. The full structural details are described herein, along with details of the synthesis of α-$Re_2X_4(dppe)_2$ (X = Cl, Br; dppe = $Ph_2PCH_2CH_2PPh_2$), complexes whose β isomers have been reported previously,[3,4] and the chemical oxidations of α-$Re_2Cl_4(LL)_2$ (LL = *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2P(CH_2)_3PPh_2$) to give paramagnetic α-$[Re_2Cl_4(LL)_2]PF_6$. This is the first time that α isomers of dirhenium(II) have been oxidized chemically.



I (α)



II (β)

Experimental Section

Starting Materials. Samples of the complexes of α-$Re_2Cl_4(dppee)_2$,[2] β-$Re_2Cl_4(dppee)_2$,[2] and α-$Re_2Cl_4(dppp)_2$ (dppp = $Ph_2P(CH_2)_3PPh_2$)[5] were prepared from $(n\text{-}Bu_4N)_2Re_2Cl_8$[6] according to the literature methods. The oxidizing agent ferrocenium hexafluorophosphate, $(Cp_2Fe)PF_6$, was obtained in the usual fashion.[7] Solvents used in the preparation and characterization of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under a nitrogen atmosphere by using standard vacuum line techniques.

A. Synthesis and Characterization of α-$Re_2X_4(dppe)_2$. (a) α-$Re_2Cl_4(dppe)_2$. A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.20 g, 0.18 mmol), dppe (0.17 g, 0.44 mmol), and methanol (20 mL), to which 10 drops of concentrated HCl had been added, was refluxed for 6 h. The resulting reaction mixture was then cooled to room temperature, and the yellow-green solid was filtered off and washed with methanol until the washings were colorless. This product was recrystallized several times from CH_2Cl_2/methanol, then chromatographed on a silica gel column (CH_2Cl_2 as eluent), and finally recrystallized from CH_2Cl_2/diethyl ether. The green product was washed with hexanes and diethyl ether and dried; yield 0.03 g (13%). Anal. Calcd for $C_{52}H_{48}Cl_4P_4Re_2$: C, 47.63; H, 3.69. Found: C, 46.54; H, 3.82. It was identified as α-$Re_2Cl_4(dppe)_2$ on the basis of its electrochemical and spectroscopic properties. The cyclic voltammogram of this complex measured in 0.1 M TBAH/CH_2Cl_2 revealed the presence of two reversible one-electron oxidations at $E_{1/2} = +0.27$ V and $E_{1/2} = +1.05$ V and an irreversible reduction at $E_{p,c} = -1.57$ V vs Ag/AgCl. These electrochemical properties are similar to those of α-$Re_2Cl_4(dppee)_2$[2] and typical of other dirhenium(II) species that contain

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