sublimation of the unchanged halide. Clearly, in contrast to later-transition-metal cyclometalation reactions, loss of HCl is a very unfavorable process for Ta(V). Work by Nugent and co-workers has shown that CH bond activation can occur at d^0-metal centers with alkoxide and amide leaving groups, although extremely high temperatures are needed.[14]

Experimental Section

All reactions and manipulations were carried out under N_2 by using Schlenk techniques. Solvents were dried by distillation over Na/benzophenone under N_2. $TaCl_5$ was purchased in resublimed form from Alfa. All phenols were dried over 4-Å molecular sieves. Lithium aryloxides were prepared from the corresponding phenol and *n*-butyllithium in hydrocarbon solvents.

$Ta(OC_6H_3Me_2\text{-}2,6)_5$ (I). The compound was easily prepared in good yield by the reaction of Li $(OC_6H_3Me_2\text{-}2,6)$ with $TaCl_5$ (6/1 ratio) in benzene over 2 h. Evaporation followed by extraction with pentane gave the pure product as a white, crystalline solid. Anal. Calcd for $TaC_{40}H_{45}O_5$: C, 61.07; H, 5.77. Found: C, 60.92; H, 5.57.

$Ta(OC_6H_3Me\text{-}t\text{-}Bu\text{-}2,6)_3Cl_2$ (II). To Li $(OC_6H_3Me\text{-}t\text{-}Bu\text{-}2,6)$ (8.25 g) suspended in benzene (300 mL) was added $TaCl_5$ (6 g). The reaction mixture was stirred overnight. The resulting suspension was then filtered to give a clear yellow filtrate. Removal of solvent and addition of hexane gave the product as a pale yellow solid, yield 9.8 g (78%). Anal. Calcd for $TaC_{33}H_{45}O_3Cl_2$: C, 53.45; H, 6.11; Cl, 9.56. Found: C, 52.90; H, 6.30; Cl, 9.32. ^1H NMR (C_6D_6, 30 °C): δ 1.42 (s, *t*-Bu), 2.50 (s, CH_3), 6.7–7.0 (m, OC_6H_3). IR spectrum (Nujol mull) between 650 and 200 cm^{-1}; 555 (s), 500 (m), 435 (s, br), 380 (w), 350 (vs, br), 318 (m), 255 (w).

$Ta(OC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6)_2Cl_3$ (III). A similar procedure using an excess of $Li(OC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6)$ gave III as a yellow powder in yields of approximately 80%. Anal. Calcd for $TaC_{24}H_{34}O_2Cl_3$: C, 44.92; H, 5.34; Cl, 16.57. Found: C, 45.18; H, 5.52; Cl, 16.38. ^1H NMR (C_6D_5CD, 30 °C): δ 1.27 (d, CMe_2), 3.58 (septet, $CHMe_2$), 6.8–7.0 (m, OC_6H_3). IR (Nujol mull) 650–200-cm^{-1} region: 650 (w), 605 (w), 595 (m), 540 (m), 430 (s), 320 (vs, br).

$Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$ (IV). A similar procedure using $Li(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)$ (excess) gave an orange suspension after stirring for 24 h. Filtration, removal of solvent, and addition of hexane gave the product as an orange solid in 30–40% yield. Recrystallization from toluene at −15 °C gave the product as large orange chunks. Anal. Calcd for $TaC_{28}H_{42}O_2Cl_3$: C, 48.19; H, 6.07; Cl, 15.24. Found: C, 48.82; H, 6.13; Cl, 14.98. ^1H NMR (C_6D_6, 30 °C): δ1.51 (s, *t*-Bu), 6.6–7.0 (m, OC_6H_3). IR (Nujol mull) 650–200-cm^{-1} region: 570 (w, sh), 540 (m), 510 (w), 463 (m), 358 (vs, br), 308 (m).

Thermolysis of $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$ (IV). A sample of IV was heated in an evacuated tube for 6–8 h in an oil bath at 170 °C. The initially orange oil began to melt to a red viscous liquid, and red crystals were slowly deposited on the cooler parts of the flask. Analysis of the sample by ^1H NMR showed only IV. Heating the sample while exposed to vacuum caused the compound to be sublimed unchanged.

Structure Determination of IV. General procedures have been described previously.[19] The position of the tantalum atom was determined from a three-dimensional Patterson map, and all remaining non-hydrogen atoms were located from a Fourier map phased on the Ta position. Hydrogen atoms were located in a subsequent difference Fourier map after several cycles of refinement and were included in all subsequent cycles. Automated ψ scans of several reflections indicated no absorption correction was necessary. A final difference Fourier map contained three peaks of intensity 0.9–1.1 e/Å^3 within 1.0 Å of the tantalum atom. All remaining peaks were less than 0.5 e/Å^3.

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Registry No. I, 82182-25-0; II, 90719-24-7; III, 90719-25-8; IV, 82190-58-7.

Supplementary Material Available: Full listings of bond distances and angles, anisotropic temperature factors, and observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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catena-Dichloro(diphenylethanedione dioxime)copper(II), a New One-Dimensional $S = {}^1/_2$ Heisenberg Chain with a Novel Zigzag Structure

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The crystal and molecular structure of the compound *catena*-dichloro(diphenylethanedione dioxime)copper(II) has been determined from single-crystal, three-dimensional X-ray diffraction data collected at room temperature. The compound $[Cu(C_{14}H_{12}N_2O_2)Cl_2]$ crystallizes as green needles in the orthorhombic space group *Pbcn* with $Z = 4$ and unit cell dimensions $a = 13.382$ (2), $b = 19.925$ (4), and $c = 6.901$ (1) Å with $D_c = 1.35$ g cm^{-3}. The structure was refined by full-matrix least-squares techniques to a conventional *R* value of 0.049. The structure may be regarded as a chain of stacked planar dichloro(diphenylethanedione dioxime)copper(II) units, with the Cu^{II} sites equidistantly arranged in zigzagged infinite chains propagating along the *c* axis and with a relatively short Cu–Cu separation of 3.649 Å. Neighboring monomeric units are linked to each other by two chloro bridges. The bridging angle Cu–Cl–Cu′ is 89.3°. Magnetic susceptibility data collected in the temperature range 2.18–18.14 K may be fit by the $S = {}^1/_2$ Heisenberg antiferromagnetic linear-chain model with the best-fit magnetic parameters J(intrachain) = −0.85 (1) cm^{-1} and $g = 2.15$ (1).

Introduction

Complexes of copper(II) chloride or copper(II) bromide with α,β-dione dioximes (α,β-H{dodo}) as chelating ligands usually crystallize in discrete dimers[2] in which monomeric units, $Cu(\alpha,\beta\text{-H}\{dodo\})X_2$, are linked together by double halide

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bridges. The intradimer exchange interaction between the paramagnetic copper(II) centers has been shown[3] to occur by superexchange[4] involving the orbitals of the bridging halide ligands. Recent systematic studies of the magnetic properties of dimeric $Cu(\alpha,\beta\text{-H}\{dodo\})X_2$ complexes have revealed that magnetic exchange effects may be controlled by means of chemical modifications of the ligands.[5]

Polymeric complexes of α,β-dione dioximes have only recently been prepared and characterized. Within the past year two examples of $Cu(\alpha,\beta\text{-H}\{dodo\})X_2$ adducts crystallizing in polymeric[6,7] chain structures have been synthesized and have been characterized by X-ray diffraction techniques. These compounds have unusual structures in which the chemical nature of the bridging functions, the magnitude of the bridging angles, and the intrachain Cu–Cu separations differ markedly.

In the present work, we describe the synthesis, X-ray structure determination, and variable-temperature magnetic susceptibility studies of dichloro(diphenylethanedione dioxime)copper(II), a compound that polymerizes to form a chain with a zigzag structure. Such a structure is rare for bis(μ-chloro)-bridged copper(II) chains.[8,9]

Experimental Section

Synthesis. Dichloro(diphenylethanedione dioxime)copper(II), $[Cu(C_{14}H_{12}N_2O_2)Cl_2]$, was prepared in a manner similar to that for the synthesis of the isomorphous dibromo counterpart.[5b] A batch of single crystals used for X-ray and magnetic investigations was obtained as follows: A 1.5-g sample of the green microcrystals was dissolved at ca. 40 °C in 150 cm^3 of a 1:1 mixture (v/v) of reagent grade propanone and diethyl ether. The green solution was filtered into a 250-cm^3 conical flask that was covered with a sheet of filter paper bearing a small hole. From a buret, dry ether was dropped slowly through this hole into the undisturbed solution during the course of 3 days. Elongated, transparent green crystals were produced. They were isolated by filtration, washed with diethyl ether, and dried in a desiccator over $CaCl_2$. The elemental microanalysis agreed well with the stoichiometric composition for a monomeric unit.

Magnetic Measurements. Magnetic susceptibility data were collected on powdered samples of $[Cu(C_{14}H_{12}N_2O_2)Cl_2]$ by using a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM) that was operated from zero field to 10 kOe by using procedures that have been described previously.[10] The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lush Model 920 MCM rotating-coil gaussmeter) were calibrated against NMR resonances (^1H and ^3Li).

The VSM system was calibrated with $HgCo(NCS)_4$.[11] Powdered samples of the compound and calibrant used in this study were contained in precision-milled Lucite sample holders. Approximately 150 mg of each was used. Diamagnetic corrections for the constituent atoms were made by using Pascal's constants, and corrections for temperature-independent paramagnetism were estimated from tabulated data.[12-14] The sum of these terms was 1.69×10^{-4} cgsu.

Table I. Crystallographic Data and Data Collection Summary for $[Cu(C_{14}H_{12}N_2O_2)Cl_2]$

fw	374.71
space group	*Pbcn*
cryst system	orthorhombic
cell dimens (291 K)	
a, Å	13.382 (2)
b, Å	19.925 (4)
c, Å	6.901 (1)
D_c, g cm^{-3}	1.35
Z	4
cryst dimens, mm	0.38 × 0.25 × 0.22
radiation	Mo Kα (λ = 0.710 69 Å)
μ, cm^{-1}	14.85
abs cor factors	none made
2θ max, deg	55
scan type	ω/θ
no. of unique data measd	2358
no. of unique data used ($F_o^2 > 3\sigma(F_o^2)$)	796
final no. of params	96
R	0.049
R_w	0.049

Table II. Atomic Coordinates for *catena*-Dichloro(diphenylethanedione dioxime)copper(II)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.0000 (1)	0.0298 (1)	0.2500 (1)
Cl	0.1069 (2)	−0.0433 (1)	0.1140 (3)
N	0.0800 (5)	0.1079 (4)	0.1587 (8)
O	0.1693 (4)	0.1035 (3)	0.0638 (7)
C(1)	0.0475 (5)	0.1683 (5)	0.1933 (9)
C(2)	0.0957 (6)	0.2306 (4)	0.1255 (12)
C(3)	0.1238 (7)	0.2796 (5)	0.2542 (14)
C(4)	0.1703 (8)	0.3353 (6)	0.1834 (17)
C(5)	0.1842 (8)	0.3461 (6)	−0.0116 (20)
C(6)	0.1548 (8)	0.2979 (7)	−0.1339 (15)
C(7)	0.1115 (7)	0.2383 (5)	−0.0708 (13)
HC(3)	0.110	0.271	0.402
HC(4)	0.198	0.374	0.274
HC(5)	0.213	0.397	−0.073
HC(6)	0.168	0.299	−0.287
HC(7)	0.088	0.198	−0.164
HO(1)	0.190	0.056	0.055

X-ray Crystallographic Studies. A green crystal of approximate dimensions (0.38 × 0.25 × 0.22 mm) was mounted on a glass fiber attached to a eucentric goniometer head. This crystal was used for all data collection at 19 °C on an Enraf-Nonius CAD-4 computer-controlled diffractometer equipped with a molybdenum X-ray tube and a graphite monochromator. The cell dimensions were determined by a least-squares refinement of the setting angles of 25 high-angle reflections. Pertinent crystallographic data are presented in Table I. Data reduction was carried out on an IBM 370 computer using a program written locally. Data were corrected for background, Lorentz and polarization factors, and a slight decomposition of the crystal over the data collection period. No absorption corrections were made; the linear absorption coefficient, μ, is 14.85 cm^{-1} for Mo Kα radiation.

The structure was solved by locating the copper atom from a Patterson function and the remaining non-hydrogen atoms and the hydroxyl hydrogen atom from successive difference Fourier syntheses. The hydrogens of the phenyl group were put in their calculated positions 1.0 Å away from the associated carbon atoms. The refinement was carried out by the full-matrix least-squares procedure, the function minimized being $\sum w[|F_o| - |F_c|]^2$. The weights, *w*, were taken to be $4F_o^2/\sigma(F_o^2)$. All atoms, except the hydrogens, were refined with anisotropic temperature factors. Hydrogen positions were kept

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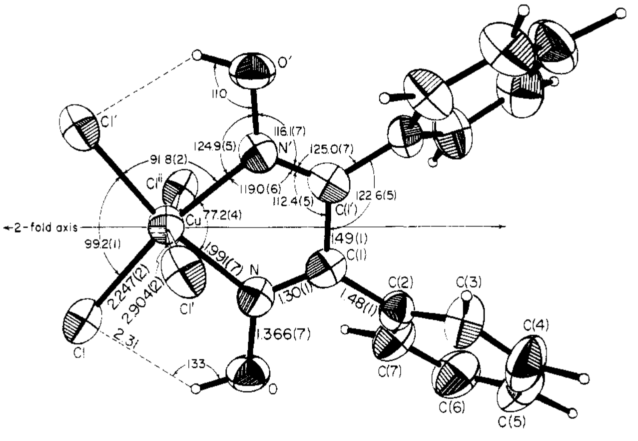


Figure 1. ORTEP drawing of the complex showing the atom-numbering scheme and pertinent bond distances and bond angles. Location of the crystallographic 2-fold axis is indicated. Dotted lines represent possible hydrogen bonds. Cl^i is related to Cl by the symmetry operation $(-x, -y, -z)$ and Cl^{ii} by $(x, -y, {}^1/_2 + z)$. The thermal ellipsoids are drawn at a 40% level. Hydrogen atoms are drawn as small circles of arbitrary size.

fixed with an isotropic B of 5.0 Å^2. As the refinement progressed, it became obvious that approximately 35 reflections with intensities greater than 3σ, which occurred in one block at the beginning of the data collection, were not measured properly. They were, therefore, removed from the data set. The final discrepancy indices

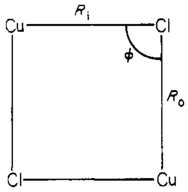
$$R = \sum||F_o| - |F_c||/\sum|F_o| \qquad R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$$

are both 0.049. The fractional coordinates are given in Table II. Tables of temperature factors and calculated and observed structure factor amplitudes are deposited as supplementary material. The atom-numbering scheme and pertinent bond distances and angles are shown in Figure 1. Drawings were produced with an IBM/370 computer using ORTEP-II.[15]

Results and Discussion

Description of the Structure. The copper(II) ion has a C_2 site symmetry. A crystallographic 2-fold axis passes through the copper ion and through the middle of the C(1)-C(1') bond of the diphenylglyoxime (DPG) ligand (Figure 1). Copper has a distorted octahedral 4 + 2 coordination with two cis chlorine atoms bonded to the copper atom at distances of 2.247 (2) Å and two cis nitrogen atoms at distances of 1.991 (7) Å, forming the "square" plane, and two chlorine atoms from two different Cu(DPG)Cl$_2$ moieties occupying the more distant axial sites at distances of 2.904 (2) Å. There are intramolecular O-H- - -Cl hydrogen bonds with an O- - -Cl distance of 2.31 Å, and an O-H- - -Cl angle of 133°.

Table III. Bridging Geometry in the Cu$_2$Cl$_2$ Plane for the Chain Compound [Cu(DPG)Cl$_2$]$_\infty$ and the Dimer [Cu(DMG)Cl$_2$]$_2$



ligand	ϕ, deg	Cu–Cu, Å	R_i, Å	R_o, Å	ref
DPG	89.3	3.649	2.247	2.904	this work
DMG	88.0	3.445	2.240	2.700	2a

Table IV. Deviations of Atoms from Least-Squares Planes through Selected Atoms[a,b]

atom	plane I	plane II	plane III
Cu	0.000	*0.000*	
Cl	*0.029*		
Cl'	*−0.029*		
N	*−0.039*	*−0.007*	
N'	*0.039*	*0.007*	
O		−0.056	
C(1)		*0.011*	0.008
C(1')		*−0.011*	
C(2)			*0.002*
C(3)			*0.018*
C(4)			*−0.024*
C(5)			*0.008*
C(6)			*0.012*
C(7)			*−0.016*

[a] Deviations that are italicized pertain to atoms used in the plane calculation. [b] Primed atoms are related to the corresponding unprimed atoms by a 2-fold axis of symmetry.

The coordination geometry about the copper ion found here is different from that found for the related complex, Cu(DMG)Cl$_2$, where DMG is dimethylglyoxime.[2a] Coordination about copper is distorted tetragonal pyramidal in Cu(DMG)Cl$_2$. A major consequence of this difference in the coordination geometry is seen in the difference in the overall copper–halogen–copper–halogen interaction. In the present complex the copper ions, separated by 3.649 (1) Å and linked together through doubly bridged Cl atoms, form a zigzag polymeric chain parallel to the c axis as shown in the stereoscopic Figure 2. The dihedral angle between the adjacent four-atom centrosymmetric planes, shown in Figure 2, is 83.6°. The structure of the DMG analogue, on the other hand, consists of discrete [Cu(DMG)Cl$_2$]$_2$ dimers. The bridging parameters for the two complexes are compared in Table III. The bridging angle Cu–Cl–Cu is 89.3° in the present complex whereas it is 88.0° in the DMG analogue. The copper-copper separation, as well as the out-of-plane copper-chlorine distance, is longer in the present complex than in the DMG analogue.

Least-squares planes through various groups of atoms are given in Table IV. The four atoms, Cl, Cl', N, and N', bonded to the copper atom are slightly out of copolanarity (plane I), but the five-atom chelate plane comprised of Cu, N, N', C(1), and C(1') is quite planar (plane II) and so is the phenyl group comprised of atoms C(2) through C(7) (plane III). The dihedral angle between the chelate plane and the phenyl group is 58.2°, and that between the two phenyl groups is 51.3°.

Other bond distances and bond angles have the usual values and are comparable to those found in Cu(DMG)Cl$_2$.[2a]

Magnetic Properties. Magnetic data plotted as magnetic moment and as inverse magnetic susceptibility vs. temperture for [Cu(DPG)Cl$_2$]$_\infty$ are shown in Figure 3 along with the best fit to the Heisenberg linear-chain results of Bonner and Fisher.[16] The Hamiltonian in eq 1 was used by Bonner and

$$H = -2J\sum_i(\hat{S}_i{}^z\hat{S}_{i+1}{}^z + \hat{S}_i{}^x S_{i+1}{}^x + \hat{S}_i{}^y\hat{S}_{i+1}{}^y) \qquad (1)$$

Fisher to generate numerical results for the temperature variation of the magnetic susceptibility of exchange-coupled $S = {}^1/_2$ ions. Hall[17] fit Bonner's numerical data to eq 2, where

$$\chi_M = (Ng^2\mu_B{}^2/kT)(0.25 + 0.14995x + 0.30094x^2) \times (1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3)^{-1} \qquad (2)$$

$x = kT/|J|$. Corrections for interchain interactions and

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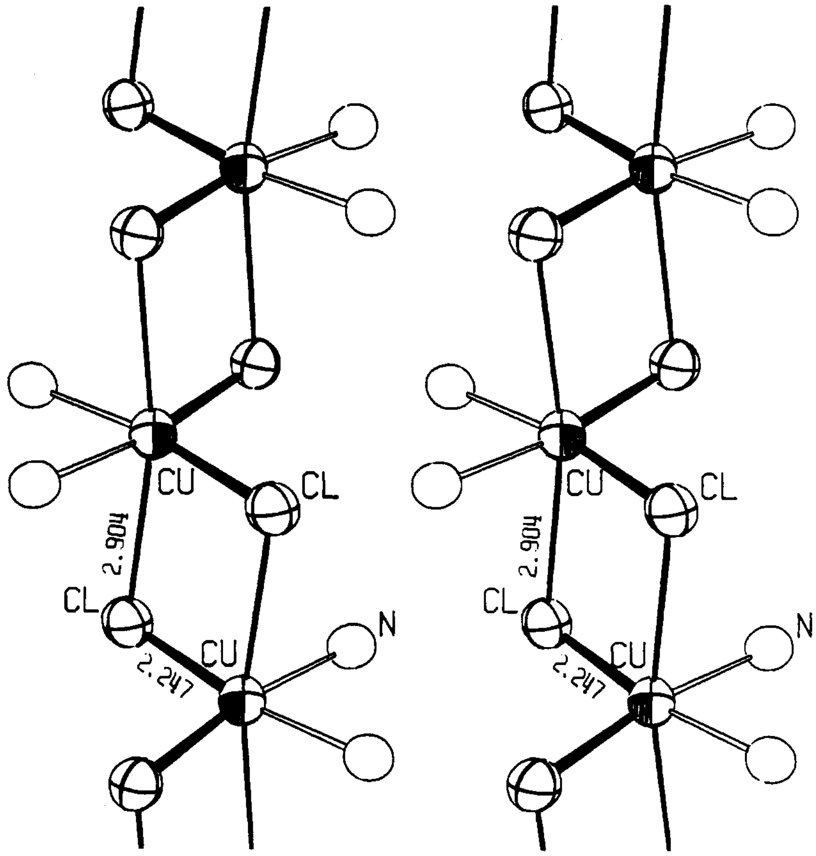

Figure 2. Stereoscopic view of the doubly bridged Cu_2Cl_2 polymeric chain running parallel to the *c* axis. There is a center of inversion in the middle of each dimeric unit. Thermal ellipsoids for the copper and chlorine atoms are drawn at a 40% probability level. The nitrogen atoms are drawn as open circles of arbitrary size.

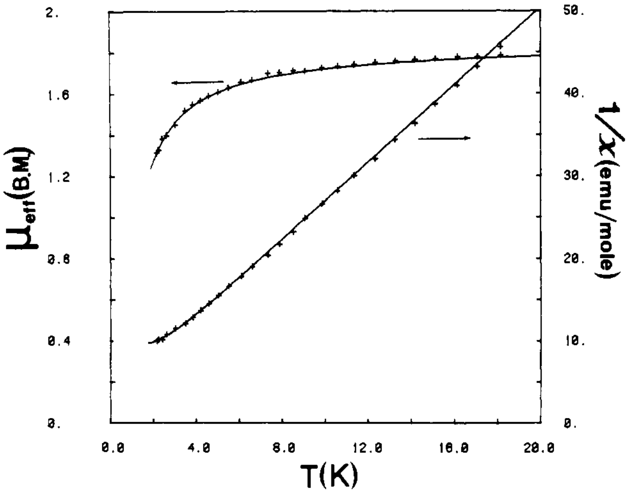

Figure 3. Magnetic data plotted as magnetic moment and inverse magnetic susceptibility vs. temperature for $[Cu(DPG)Cl_2]_\infty$. The solid line was the best fit to the Heisenberg linear-chain model with the parameters J(intrachain) = −0.85 (1) cm^{-1}, g = 2.15 (1), percent impurity = 0.0, and J'(interchain) = 0.0 cm^{-1}.

paramagnetic impurities were found to be unnecessary.

The resultant equation for $\chi_{Cu}{}^{cor}$ was fitted to the data by using a nonlinear Simplex fitting routine using as the criterion of best fit the minimum value of

$$\sum_i (\chi_i{}^{calcd} - \chi_i{}^{obsd})^2/(\chi_i{}^{obsd})^2$$

The best-fit magnetic parameters are J(intrachain) = −0.85 (1) cm^{-1} and g = 2.15 (1). The negative J value is indicative of antiferromagnetic intrachain interactions consistent with the bond distances and angles in the exchange-coupled Cu_2Cl_2 unit. The magnetic moment was calculated from the expression

$$\mu_{eff} = 2.828(\chi_{Cu}{}^{cor}T)^{1/2}$$

The solid lines in Figure 3 were generated with the best-fit parameters given above.

Structural and Magnetic Correlations. There is now a considerable body of data for stacked, ligand-bridged copper(II) dimers and chains which reveal that the exchange coupling constant is a function of the angle at the ligand bridge, ϕ, and the length of the superexchange pathway.[18] Relatively smooth correlations of J with the quotient ϕ/R_0 (where R_0 is the long bond distance in the Cu_2X_2 exchange-coupled unit) exist for chloro- and sulfur-bridged copper(II) complexes.

The ϕ/R_0 value for the Cu_2Cl_2 unit in $[Cu(DPG)Cl_2]_\infty$ is 30.75°/Å (ϕ = 89.3°, R_0 = 2.904 Å), a value that is similar to the ϕ/R_0 value of 30.65°/Å (ϕ = 91.89°, R_0 = 2.998 Å) in $[Cu(thiazole)_2Cl_2]_\infty$.[19] The exchange coupling constant J for $[Cu(thiazole)_2Cl_2]_\infty$ is −3.7 cm^{-1}. The difference in the exchange coupling constants for these two compounds with nearly equal ϕ/R_0 values is probably the result of an additional structural variation in the zigzag chain compound. As shown in Figure 2, adjacent Cu_2Cl_2 units lie in planes that are nearly mutually perpendicular. The Cu_2Cl_2 exchange-coupled units are coplanar in $[Cu(thiazole)_2Cl_2]_\infty$ and other typical chain compounds such as $[Cu(py)_2Cl_2]_\infty$.[20]

Current models for superexchange focus attention on relative orientations of exchange-coupled units, and the influence of the angle between the planes on the exchange is of interest.

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Adjacent planes are also mutually perpendicular in the alternating chain compound [Cu(3,6-dithiaoctane)Cl_2]$_\infty$, and although the exchange coupling constants were negative as expected, the absolute magnitudes of the coupling constants were smaller than expected.[21] That observation, coupled with the results of the present work, suggests that the relative orientation of the Cu_2X_2 planes in chain compounds is important in determining the sign and magnitude of the exchange coupling constant. It appears that ferromagnetic contributions predominate when adjacent Cu_2X_2 planes are mutually perpendicular or nearly perpendicular. Additional data on other compounds with this structural feature must be collected so that this effect can be understood.

Although the out-of-plane Cu···Cl interatomic separation is relatively long, it is the shortest bond distance in such bis(μ-chloro)-bridged copper(II) chain compounds.[18] The longest comparable copper–chloride separation in an exchange-coupled chain is 3.21 Å in [Cu(4-Etpy)$_2Cl_2$]$_\infty$,[22] while the longest such distance in a dimeric chloride-bridged molecule is 3.37 Å in [Cu(2-Mepy)$_2Cl_2$]$_2$.[23] It is clear that exchange interactions in these compounds can be transmitted through long interatomic separations.

It has been pointed out that a universal ϕ/R_0 correlation for a series of chemically and structurally related complexes is unexpected and that the magnetic and structural correlation should involve a family of J vs. ϕ/R_0 curves.[18] Such a family of curves would lead to a surface as described by Willett and co-workers.[24]

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Supplementary Material Available: Tables of temperature factors and calculated and observed structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Synthesis and Structures of Compounds Containing Double Bonds between the Heavier Group 5A Elements: Diphosphenes, Diarsenes, Phosphaarsenes, and Phosphastibenes

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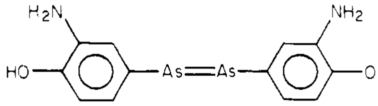
The syntheses of the symmetrical diphosphene $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**2**), the unsymmetrical diphosphenes [2,4,6-(t-Bu)$_3C_6H_2$]P=PC$(SiMe_3)_3$ (**5**) and [2,4,6-(t-Bu)$_3C_6H_2$]P=PCH$(SiMe_3)_2$ (**7**), the phosphaarsene [2,4,6-(t-Bu)$_3C_6H_2$]P=AsCH$(SiMe_3)_2$ (**12**), the phosphastibene [2,4,6-(t-Bu)$_3C_6H_2$]P=SbCH$(SiMe_3)_2$ (**14**), and the diarsene [2,4,6-(t-Bu)$_3C_6H_2$]As=AsCH$(SiMe_3)_2$ (**18**) are described. X-ray diffraction studies have been performed on **2**, **12**, and **18**. Diphosphene **2** crystallizes in space group $P\bar{1}$ (No. 2) with a = 15.629 (7) Å, b = 9.155 (5) Å, c = 12.486 (6) Å, α = 91.58 (4)°, β = 111.42 (5)°, and γ = 90.02 (4)°. Phosphaarsene **12** crystallizes in space group $P\bar{1}$ (No. 2) with a = 9.991 (4) Å, b = 10.452 (9) Å, c = 15.140 (15) Å, α = 89.72 (7)°, β = 85.03 (5)°, and γ = 77.72 (5)°. Diarsene **18** crystallizes in space group $P\bar{1}$ (No. 2) with a = 9.955 (9) Å, b = 10.393 (7) Å, c = 15.159 (5) Å, α = 89.56 (4)°, β = 85.39 (6)°, and γ = 78.31 (9)°. The nature of the bonding in these and related double-bonded compounds is discussed with use of the available molecular structural and electronic spectral information. An extensive compilation of ^{31}P NMR spectroscopic data is presented and discussed.

Introduction

The history of the present subject dates back to 1877, when Köhler and Michaelis[1] treated $C_6H_5PH_2$ with $C_6H_5PCl_2$ and isolated a compound of empirical composition C_6H_5P, which they dubbed "phosphobenzene" and formulated as $C_6H_5P{=}PC_6H_5$ by analogy with azobenzene. This field lay essentially dormant until 1957, when, in a pioneering study, Mahler and Burg[2] reported the preparation of the cyclopolyphosphines $(CF_3P)_4$ and $(CF_3P)_5$ and suggested an oligomeric structure for "phosphobenzene". This postulate was confirmed almost simultaneously by Kuchen and Buchwald[3] on the basis of molecular weight measurements. Subsequent X-ray diffraction studies have revealed that "phosphobenzene" adopts pentameric or hexameric structures in the solid state.[4] A somewhat similar situation arose with arsenicals. Thus, Erlich,[5] the originator of the chemotherapeutic drug "Salvarsan", formulated his compound as



but once again, X-ray crystallographic work indicated that, e.g., compounds of empirical composition C_6H_5As are, in fact, oligomeric.[6]

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