Registry No. I, 58689-52-4; II, 58657-89-9; [Cu(p_3)(BH_4)], 60294-97-5; [Co(p_3)(NO)], 60294-98-6; [Ni(p_3)(CS_2)], 60294-99-7; [Co(p_3)(BD_4)], 60295-00-3; [Cu(p_3)Cl], 37701-76-1; [Ni(p_3)$_2$], 60295-01-4.

Supplementary Material Available: Listings of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Mixed-Valence Copper Complex Trichlorobis(4-methyl-1,8-naphthyridine)dicopper

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The binuclear complex trichlorobis(4-methyl-1,8-naphthyridine)dicopper has been prepared and characterized by x-ray diffraction and ESR spectroscopy. The emerald green crystals conform to monoclinic space group $P2_1/c$ with $a = 11.795$ (5), $b = 14.850$ (5), $c = 11.320$ (5) Å, $\beta = 99.20$ (9)°, $Z = 4$. The structure, refined to a final conventional R value of 0.051 on 2815 counter data, consists of dimeric molecules containing two equivalent copper atoms in pseudotetrahedral environments, bridged by one chlorine atom and by two 4-methyl-1,8-naphthyridine ligands, which act as bidentate bimetallic ligands. The equivalence of the two copper atoms is substantiated by the ESR spectra. The electronic structure of the complex is also discussed.

Introduction

Recently we have reported that the potentially bidentate ligand 1,8-naphthyridine (NN) and its 4-methyl-substituted derivative (MeNN) form binuclear complexes [Ni_2X_2(NN)$_4$]Y and [Ni_2X_2(MeNN)$_4$]Y (X = Cl, Br, I, NO_3, NCS; Y = PF_6, B(C_6H_5)$_4$) in which the oxidation number of the nickel atoms is +1.5.[1,2] These complexes have been found to have a dimeric structure of the copper acetate type, with the nonlinear triatomic group N–C–N of NN and MeNN acting as a syn-syn bridge between two equivalent nickel atoms.

Encouraged by these results we have investigated the behavior of naphthyridine ligands toward copper(II) salts. Several copper(I) and copper(II) complexes with NN and some methyl derivatives have been reported,[3-7] but in no instance were the ligands found to bridge two metal atoms. We have now found that by reaction of copper(II) chloride with MeNN in alcoholic medium a mixed valence compound of formula [Cu_2Cl_3(MeNN)$_2$] is formed, and we wish to report its characterization by single-crystal x-ray diffractometry and by ESR spectroscopy.

Experimental Section

Preparation of the Complex. The materials and solvents were reagent grade and were used without further purification. The ligand MeNN was prepared according to the reported procedure.[8] To a hot (50 °C) solution of 1 mmol of $CuCl_2 \cdot 2H_2O$ in 20 cm^3 of *n*-butyl alcohol a solution containing 2 mmol of the ligand in 5 cm^3 of the same solvent was added and the reaction mixture was brought to the boiling point. A green emerald crystalline precipitate was formed, which was filtered, washed with *n*-butyl alcohol and petroleum ether, recrystallized from a mixture of *n*-butyl alcohol and dichloromethane, and dried in a vacuum oven at 60 °C. *Anal.* Calcd for $C_{22}H_{16}Cl_3Cu_2N_4$: C, 41.63; H, 3.24; Cl, 20,85; Cu, 24.06; N, 10.76. Found: C, 41.43; H, 3.08; Cl, 20.38; Cu, 24.36; N, 10.73.

Collection and Reduction of the X-Ray Intensity Data. The compound [Cu_2Cl_3(MeNN)$_2$] crystallizes as dark green prisms, which are ill-shaped, showing large cavities at least on one side. One crystal of dimensions 0.52 × 0.16 × 0.14 mm^3 was chosen for the preliminary work of orientation, lattice constants, and space group determination and finally for data collection. These routines were executed by a Philips PW 1100 automated diffractometer. The compound was found to be monoclinic with space group $P2_1/c$. The cell constants were determined (at ca. 22 °C) as $a = 11.795$ (5), $b = 14.850$ (5), $c =$

Table I. Positional and Thermal Parameters[a] for the Atoms of $[Cu_2Cl_3(MeNN)_2]$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.3386 (2)	0.0657 (3)	0.2102 (3)	0.049 (2)	0.045 (2)	0.103 (3)	−0.006 (2)	0.038 (2)	−0.007 (2)
Cu(2)	0.1920 (2)	0.0675 (3)	0.3331 (3)	0.045 (2)	0.043 (2)	0.094 (3)	0.004 (2)	0.031 (2)	0.002 (2)
Cl(1)	0.4734 (6)	0.1100 (5)	0.1038 (7)	0.084 (5)	0.064 (5)	0.145 (7)	−0.014 (4)	0.076 (5)	−0.010 (5)
Cl(2)	0.0704 (6)	0.1124 (5)	0.4529 (7)	0.087 (5)	0.051 (4)	0.147 (7)	0.082 (4)	0.077 (5)	−0.002 (4)
Cl(3)	0.2500 (5)	0.1919 (3)	0.2523 (7)	0.046 (3)	0.039 (3)	0.134 (6)	0.004 (3)	0.034 (4)	0.008 (5)
N(1)	0.4264 (13)	−0.0246 (11)	0.3308 (16)	0.033 (9)	0.038 (12)	0.070 (14)	0.003 (9)	−0.005 (11)	−0.014 (9)
N(2)	0.2712 (13)	−0.0375 (11)	0.4260 (15)	0.039 (9)	0.033 (13)	0.075 (13)	0.002 (8)	0.011 (11)	0.001 (9)
N(3)	0.0893 (13)	−0.0185 (12)	0.2043 (17)	0.024 (9)	0.062 (14)	0.075 (14)	0.006 (9)	0.016 (10)	0.016 (11)
N(4)	0.2368 (12)	−0.0218 (11)	0.0955 (14)	0.033 (9)	0.043 (12)	0.058 (12)	−0.002 (9)	0.011 (9)	−0.006 (9)
C(6)	0.4261 (21)	−0.2555 (18)	0.6416 (22)	0.092 (20)	0.090 (21)	0.108 (21)	−0.011 (16)	−0.020 (12)	0.017 (17)
C(16)	0.0682 (18)	−0.2226 (17)	−0.1474 (20)	0.058 (15)	0.085 (19)	0.098 (19)	0.002 (13)	0.028 (15)	0.009 (16)

Atom	x/a	y/b	z/c	U, Å^2	Atom	x/a	y/b	z/c	U, Å^2
C(1)	0.5332 (18)	−0.0490 (16)	0.3122 (19)	0.057 (6)	C(11)	−0.0148 (18)	−0.0450 (15)	0.2205 (19)	0.055 (6)
C(2)	0.5900 (17)	−0.1191 (15)	0.3833 (20)	0.058 (7)	C(12)	−0.0791 (17)	−0.1063 (15)	0.1522 (20)	0.054 (7)
C(3)	0.5438 (17)	−0.1634 (15)	0.4643 (18)	0.051 (6)	C(13)	−0.0425 (17)	−0.1434 (14)	0.0581 (18)	0.051 (6)
C(4)	0.4352 (18)	−0.1390 (14)	0.4810 (20)	0.049 (7)	C(14)	0.0694 (17)	−0.1188 (15)	0.0268 (20)	0.053 (6)
C(5)	0.3719 (17)	−0.1775 (16)	0.5634 (20)	0.063 (7)	C(15)	0.1231 (18)	−0.1530 (16)	−0.0600 (20)	0.061 (7)
C(7)	0.2656 (21)	−0.1481 (17)	0.5739 (21)	0.064 (6)	C(17)	0.2306 (17)	−0.1193 (14)	−0.0729 (19)	0.059 (6)
C(8)	0.2195 (17)	−0.0769 (15)	0.5065 (19)	0.060 (6)	C(18)	0.2785 (18)	−0.0565 (17)	0.0049 (20)	0.058 (6)
C(9)	0.3788 (17)	−0.0676 (17)	0.4136 (18)	0.044 (6)	C(19)	0.1297 (17)	−0.0528 (16)	0.1102 (19)	0.050 (6)

[a] The anisotropic thermal parameters are of the form: $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 - c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl]$.

11.320 (5) Å, β = 99.20 (9)°, using Mo Kα radiation monochromatized by a flat graphite crystal (λ 0.7093 Å). The values of the lattice constants given above are those obtained as averages from different refinements of the orientation matrix (UB) based on a set of 16 orienting reflections which were centered 12 times prior to and during data collection. The standard deviations (given as sample standard deviation, $s = [(x_i - \bar{x})^2/(N-1)]^{1/2}$) have somewhat high values, which are attributable to the poor crystalline quality of the specimen; this seems also the cause of the observed spreading and splitting of most reflections and it is probably a common feature for compounds containing bridging NN and metal atoms in mixed valence states.[2]

The density value obtained by flotation is in agreement with the calculated value for four dimeric molecules of formula $C_{22}H_{16}Cl_3Cu_2N_4$ in the unit cell (d_{measd} = 1.56 (3) g/cm^3, d_{calcd} = 1.58 g/cm^3). The identifiable faces of the crystal were {101}, {$\bar{1}0\bar{1}$}, {$\bar{1}01$}, {$10\bar{1}$}, {010}, and {$0\bar{1}0$}. Intensity data were collected at a take-off angle of 2°, The θ–2θ scan technique was employed with a scan range of 0.70° in θ, corrected for dispersion, at a scan rate of 0.05°/s. The background measuring time at each side of the scan was determined as scan time/2. Weak reflections were scanned up to a maximum of three times. A total of 2815 intensities were recorded up to θ = 20°. The intensities of three standard reflections, measured every 2 h, showed only the deviation from the mean predicted from counting statistics. Slight misalignments of the crystal, which occurred during the data collection, were overridden by automatic reorientation of the specimen. Data processing was carried out as previously described,[10] a value of 0.04 being assigned to the instability factor R, used in the formula to derive the $\sigma(I)$'s. Lorentz–polarization and absorption corrections were applied to the intensities. The linear absorption coefficient for this compound is 25.84 cm^{-1} and for the crystal chosen the transmission coefficients evaluated by numerical integration were found to range from 0.631 to 0.715. Allowance must be made for the fact that these coefficients may be affected by errors due to the imprecise description of the crystal form. A total of 864 reflections were greater than three times their estimated standard deviations.

Solution and Refinement of the Structure. The structure was solved by direct methods using the program MULTAN.[11] Of the 27 nonhydrogen atoms contained in the asymmetric unit only five carbon atoms could not be detected in the initial E map. A Fourier synthesis allowed the completion of the model, which gave an R factor of 18.9, $R = 100\sum(||F_o| - |F_c||)/\sum|F_o|$. Least-squares refinement of the positional and thermal isotropic parameters converged to R = 9.8 after two cycles (with R_w = 10.7, where $R_w = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and $w = 1/\sigma^2(F_o)$. Two more least-squares cycles using anisotropic thermal parameters for Cu, Cl, and N atoms and the two carbon atoms of the methyl groups attached to the aromatic rings reduced R to 6.1 and R_w to 7.0. A difference Fourier map clearly showed several hydrogen atoms, which were introduced at calculated positions in the next stage of LS refinement. The hydrogen atoms belonging to the methyl groups were introduced at positions obtained as the best fitting of idealized models to partial models derived from the ΔF map. A final LS cycle, in which the effects of anomalous dispersion $\Delta f'$ and $\Delta f''$ for Cu and Cl species were taken into account in the calculation of F_c's, gave an R equal to 5.1 and R_w equal to 5.9. The final positional and thermal parameters for $[Cu_2Cl_3(MeNN)_2]$ are given in Table I. The list of observed and calculated structure factors is available as supplementary material.

Instrumentation. Solution and solid state absorption spectra and magnetic susceptibility values were obtained as previously described.[12]

ESR Spectra. The ESR spectra were obtained with a Varian E-9 spectrometer operating at X-band frequency equipped with a Varian E-257 variable temperature accessory. Frozen solutions in CH_2Cl_2 were obtained by pouring the solution directly into liquid nitrogen since several attempts to obtain satisfactory glasses, also by using mixtures of solvents, were unsuccessful due to crystallization of the compound.

Results and Discussion

Synthesis of the Complex. 1,8-Naphthyridine and some of its methyl derivatives have been found to stabilize low, integral[7] or mixed,[1,2] valence states of nickel and copper. In the formation of these complexes the starting materials were nickel(II) and copper(II) salts. The reductions, which occurred in the absence of any specific reducing agent, were related to the presence of tetraphenylborate anions[1,2] or to some impurities in the drying agent.[7] The present complex $[Cu_2Cl_3(MeNN)_2]$ is obtained in n-butyl alcohol, no one of the above suggested reducing agents being present in the reaction mixture.

Therefore the reduction of the metal is very likely to be connected with the presence of the ligand, either alone or in cooperation with the solvent or other agents present in the mixture.

The complex is sparingly soluble in all the common organic solvents, the best ones being dichloromethane and 1,2-dichloroethane. The spectra in the solid and in solution are quite similar to each other, as shown in Figure 1. They consist of an intense band with a maximum at 1.46 μm^{-1} and two less intense bands with a maximum at 1.03 and a shoulder at ca. 0.8 μm^{-1}. The magnetic moment for the dimeric units $[Cu_2Cl_3(MeNN)_2]$ is 1.99 μ_B, corresponding to the presence of one unpaired electron per two copper atoms.

Crystal Structure Description. The structure of $[Cu_2Cl_3(MeNN)_2]$ shown in Figure 2 consists of neutral dimeric molecules, four per unit cell, where the two copper atoms are bridged by a chlorine atom and by the two MeNN

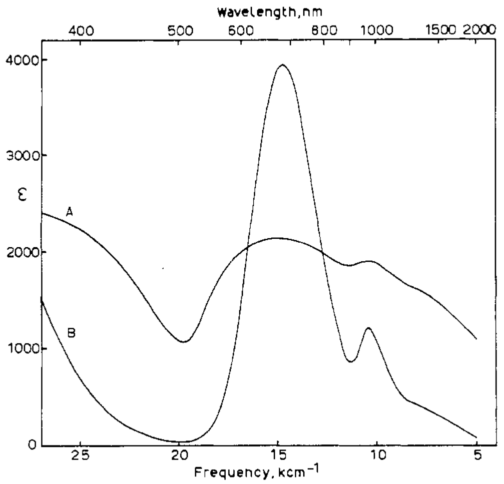

Figure 1. Electronic spectra of $[Cu_2Cl_3(MeNN)_2]$ (A) solid and (B) 1,2-dichloroethane solution. The molar extinction coefficient is referred to a dimeric moiety.

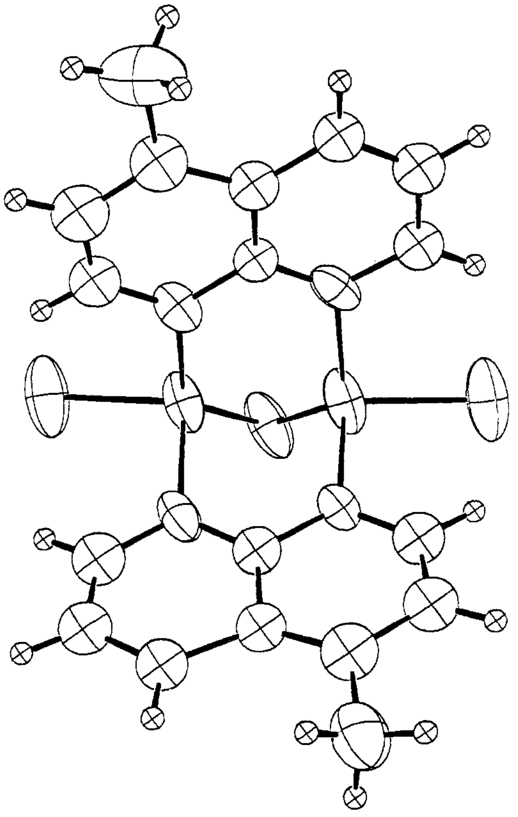

Figure 2. A view of the complex $[Cu_2Cl_3(MeNN)_2]$ (ORTEP diagram showing 50% probability ellipsoids).

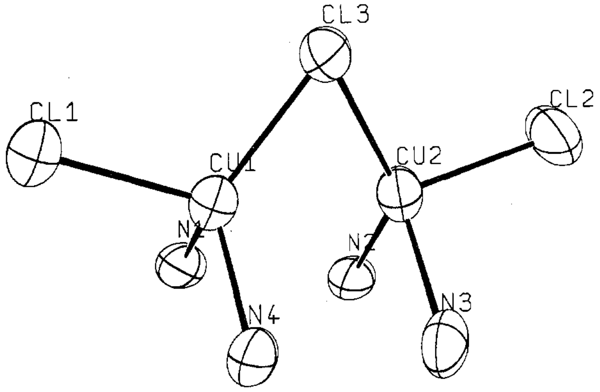

Figure 3. Perspective view of the immediate inner coordination sphere in $[Cu_2Cl_3(MeNN)_2]$.

Table II. Distances (Å) and Angles (deg) within the Coordination Sphere

Cu(1)-Cu(2)	2.386 (4)	Cu(2)-Cu(1)-Cl(1)	162.3 (3)
Cu(1)-Cl(1)	2.242 (8)	Cu(1)-Cu(2)-Cl(2)	162.8 (2)
Cu(1)-Cl(3)	2.233 (6)	Cu(1)-Cl(3)-Cu(2)	64.8 (2)
Cu(2)-Cl(2)	2.228 (8)	Cl(1)-Cu(1)-Cl(3)	105.4 (3)
Cu(2)-Cl(3)	2.218 (7)	N(1)-Cu(1)-Cl(1)	102.8 (5)
Cu(1)-N(1)	2.078 (15)	N(1)-Cu(1)-Cl(3)	127.2 (5)
Cu(1)-N(4)	2.070 (16)	N(1)-Cu(1)-N(4)	100.6 (6)
Cu(2)-N(3)	2.159 (17)	N(4)-Cu(1)-Cl(1)	103.7 (5)
Cu(2)-N(2)	2.024 (16)	N(4)-Cu(1)-Cl(3)	114.5 (5)
		Cl(2)-Cu(2)-Cl(3)	105.8 (3)
		N(2)-Cu(2)-Cl(2)	102.7 (5)
		N(2)-Cu(2)-Cl(3)	135.2 (5)
		N(2)-Cu(2)-N(3)	93.3 (7)
		N(3)-Cu(2)-Cl(2)	104.0 (5)
		N(3)-Cu(2)-Cl(3)	113.0 (5)

molecules. Figure 3 summarizes the important features of the copper coordination geometry and shows the atom numbering scheme. Figure 4 gives an overall stereoscopic view of the contents of the unit cell. Figure 5 gives a summary of bond distances and angles within the two independent MeNN molecules.

The coordination geometry about each copper atom can be described as a highly distorted tetrahedron, defined by two chlorine atoms, one bridging and one terminal, and two nitrogen atoms from different MeNN molecules. The present is the second observation of the binucleating capacity of naphthyridines in conjunction with reduction of the metal to an unusual mixed valence state. Selected intramolecular bond distances and angles are reported in Table II. The six angles L-Cu-L′ within each tetrahedral moiety range from 127.2 to 100.6° for Cu(1) and from 135.2 to 93.3° for Cu(2). The angles larger than the tetrahedral value on each center are the two involving the bridging chlorine atom and the nitrogen donors. Therefore the distortion from tetrahedral geometry cannot be described here as flattened, a common feature otherwise observed in most copper(II) tetrahedral complexes.[13]

All the four Cu-Cl bonds are equal within error, no appreciable difference being observed between bridging and terminal bonds. The copper-nitrogen distances at site 1 are practically equal to each other, while a difference of about 0.14 Å is observed between the Cu-N distances (2.16-2.02 Å) at site 2. The observed difference seems hardly attributable to any difference in the electronic configurations of the two copper atoms but rather to the steric requirements of the bridged structure. This interpretation is endorsed by the observed symmetry of the chloride bridge and by the ESR spectra discussed in the following section. Dimerization of tetrahedral copper(I) attained through a strain of nitrogenous ligands such as those belonging to the hydrotrispyrazolylborate type[14] is observed to lead to a variety of Cu-N interactions as short as 1.931 or as long as 2.777 Å.

The Cu-Cu contact of 2.38 Å is short enough to suggest the possibility of some overlap of metal orbitals and compares well with those found in the copper(I) and in the copper(II) dimers with 1,3-diphenyltriazene (dpt), i.e., 2.451 Å in $[Cu_2(dpt)_2]$[15] and 2.441 Å in $[Cu_2(dpt)_4]$.[16] Another type of ligand structurally similar to MeNN which can form copper(II) dimers with the same bridging N-C-N group is that of the nucleotide bases such as adenine (AdH),[17] its anionic (Ad)[18] or cationic (AdH_2)[19] derivatives, as well as hypoxanthyne.[20] The Cu-Cu distances in these types of compounds fall in the range 2.95-3.02 Å. The shorter bite and the parallelism (the angle between the N-Cu-N planes is 5.1°) of the bonding orbitals of the nitrogen atoms of the

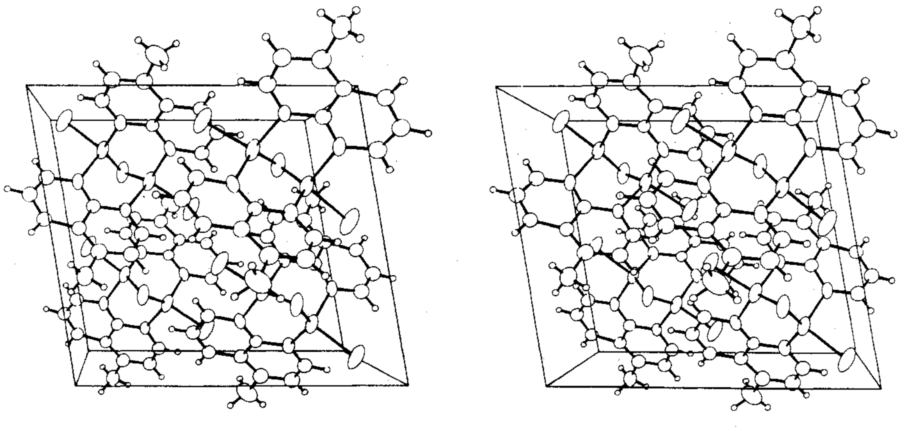

Figure 4. Stereoscopic view of the contents of the unit cell in $[Cu_2Cl_3(MeNN)_2]$.

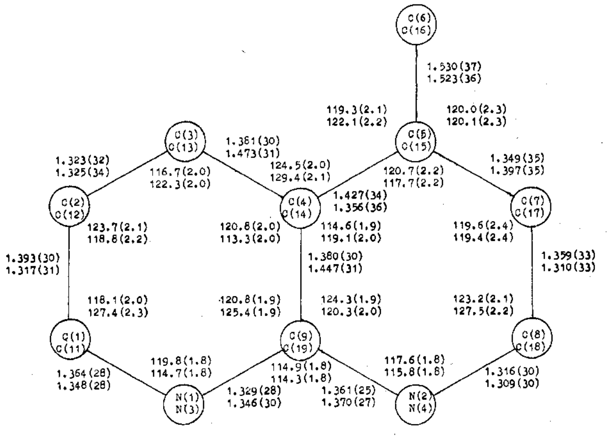

Figure 5. Summary of bond distances (Å) and angles (deg) in MeNN ligand molecules.

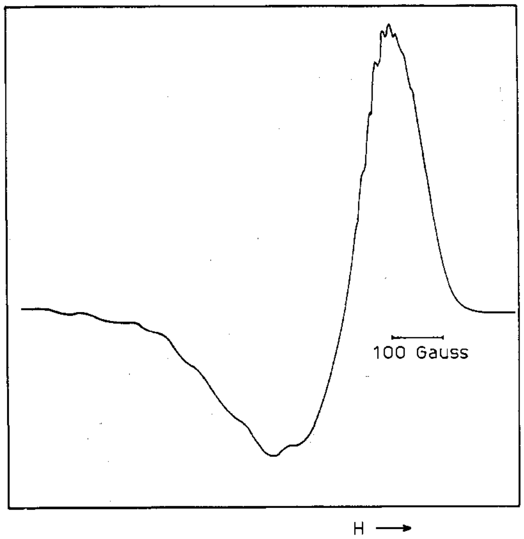

Figure 6. ESR spectrum of a frozen solution of $[Cu_2Cl_3(MeNN)_2]$ in 1,2-dichloroethane at liquid nitrogen temperature.

MeNN molecule may favor a significantly shorter Cu–Cu distance in the present compound.

ESR Data. The frozen solution spectra of $[Cu_2Cl_3(MeNN)_2]$ in dichloromethane are reported in Figure 6. The isotropic spectrum consists of a broad featureless band centered at $g_{iso} = 2.14$. The frozen solution spectra, however, show a larger number of details and can be interpreted using the effective Hamiltonian

$$H = \mu_B \mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$$

with $\mathbf{S} = {}^1/_2$, $\mathbf{I} = \sum \mathbf{I}_i$, where $\mathbf{I}_i$ is the nuclear spin of each of the two equivalent copper atoms.[21] The difference between ^{63}Cu and ^{65}Cu has been neglected. The **g** and **A** tensors are to be considered as completely anisotropic.

The overall appearance of the spectrum is not very dissimilar from that observed for low symmetry distorted octahedral or tetrahedral copper(II) complexes,[13] with g_3, corresponding to $g_{\|}$ of axial symmetry, larger than g_1 and g_2, corresponding to $g_{\perp}$. The main difference from the spectra of copper(II) complexes is that each line is split by hyperfine interaction into seven components attributable to the interaction with the two equivalent nuclei. The lines corresponding to g_3 are broad and partially overlap the g_1 and g_2 lines in the high-field region; however, the ratios of the intensities of the individual lines seem to conform to those expected for two equivalent nuclei. The hyperfine lines of g_1 and g_2 are narrower and they also overlap each other partially. Since the symmetry of the complex, as shown by the crystal data, must be low, at best C_{2v}, the **g** and **A** tensor axes are not expected to be parallel. Under these circumstances the computer simulation of the spectra becomes unduly complicated; therefore we extracted the relevant spin Hamiltonian parameters directly by inspection of the spectra. The chosen values are: $g_1 = 2.02$, $g_2 = 2.07$, $g_3 = 2.33$, $A_1 = 16$ G, $A_2 = 13$ G, $A_3 = 72$ G. For each of these values the estimated error is one digit on the last figure. The average g value corresponds closely to g_{iso} of the fluid solution.

These values compare well with those reported for another binuclear mixed valence copper complex[22] and are similar to those usually found for copper(II) complexes in tetrahedral, square planar, or intermediate distorted arrangements. The values of the hyperfine coupling constants are small, about half of the value usually found in copper(II) complexes,[23] as expected for the delocalization of the unpaired electron on two equivalent centers.[24]

Electronic Structure of the Complex. From the above data it appears that both the x-ray analysis and the ESR spectra concur to assign the $[Cu_2Cl_3(MeNN)_2]$ complex to Robin and Day's class III-A for mixed valence compounds.[25] In this framework the electronic levels can be adequately described only in a molecular orbital model extended to both the equivalent metal atoms. It is generally recognized[26] however that for dimeric copper complexes the weakly coupled chromophore[27] model may provide a sufficiently good description of the energy levels. The energies of the metal d orbitals can be considered well separated in energy from those of the ligand orbitals, and the splitting of the levels of an individual copper atom induced by the presence of the second equivalent moiety can be considered small. Therefore the unpaired electron must be in an orbital which extends over all the dimer, and the spectrum of levels does not differ markedly from that of a corresponding copper(II) complex. As a matter of fact electronic transitions are observed at 0.8

and 1.03 μm^{-1} which, for intensity and energy, correspond to d–d transitions of distorted tetrahedral copper(II) complexes. Also the ESR data, with the high g_3 value of the hyperfine coupling constant, conform to this view, since it has been suggested that these are the features which characterize tetrahedral copper(II) complexes.[28]

The band at 1.46 μm^{-1} in the electronic spectra is very intense and can be assigned to a charge transfer transition, presumably involving the metals and the system of the MeNN and chloride ligands.[29] A low-energy transition was observed also in the mixed valence complexes $[Ni_2X_2(NN)_4]^+$ and it was found to possess polarization properties compatible with Ni–NN charge transfer nature.[2] Since no such band is observed in the corresponding monomeric nickel(II) and copper(II) complexes the lowering of the energy of the absorption can be ascribed to the reduced charge on the metal in the mixed valence compound and to the formation of the dimer.[26]

An alternative interpretation of the spectra may be that the equivalence of the two copper atoms is not retained in the instantaneous vision provided by the electronic specta, a fact similar to that commonly observed in Jahn–Teller distorted copper(II) ions.[30] In this case the 1.46 kcm^{-1} band might be due to an intervalence transition, making the complex, as regards the electronic spectra, a class II mixed valence compound.[29] It is worth noting however that the polarization properties of the mixed valence nickel compound do not confirm this assignment.

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Supplementary Material Available: A listing of structure factor amplitudes (5 pages). Ordering information can be found on any current masthead page.

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Synthesis and Structure of Hexamolybdobis(organoarsonates)

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Five salts of the heteropoly molybdate anion $(RAs)_2Mo_6O_{24}^{4-}$ (R = CH_3, C_6H_5, p-$C_6H_4NH_2$) have been synthesized and characterized by spectroscopic measurements. The complexes are stable in aqueous solutions at pH 3–5. The structure of $[(CH_3)_4N]_2Na_2[(CH_3As)_2Mo_6O_{24}]\cdot 6H_2O$ ($P\bar{1}$; $a = 11.712\ (2)$ Å, $b = 11.589\ (1)$ Å, $c = 8.331\ (1)$ Å, $\alpha = 87.84\ (1)°$, $\beta = 110.31\ (1)°$; $\gamma = 112.13\ (1)°$) has been determined by single-crystal x-ray diffraction. Final consistency indices of 0.043 ($R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$) and 0.072 ($R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were obtained. The structure of the anion is closely related to that previously reported for $(CH_3P)_2Mo_5O_{21}^{4-}$ and consists of a ring of six edge-shared MoO_6 octahedra capped above and below by the $CH_3AsO_3^{2-}$ groups.

Introduction

As part of our program to investigate the chemistry of organic derivatives of heteropolyoxometalate complexes, we have previously described molybdenum complexes of monoalkyl- and monoarylphosphonates, RPO_3^{2-}, and dialkyl- and diarylarsinates, $R_2AsO_2^-$. We now report the syntheses, solution properties, and structures of a series of polymolybdate anions based on monoalkyl- and monoarylarsonates, $RAsO_3^{2-}$. In 1913[1] Rosenheim and Bilecki isolated organic derivatives of this type with $RAsO_3^{2-}$:MoO_3 ratios of 1:3, 1:6, 1:9, and 2:9. In addition, the existence of 2:2, 2:5, and 1:9 complexes of methylarsonate and molybdate have been claimed on the basis of solution studies.[2,3]

We have prepared several examples of two series of complexes with the As:Mo ratio 1:3 and in this paper we describe those complexes with the general formula $(RAs)_2Mo_6O_{24}^{4-}$. Very recently Filowitz and Klemperer[4] have reported the phenyl derivative of this series and proposed its structure from the ^{17}O NMR spectrum.

Experimental Section

Preparation of Complexes. Hexamolybdobis(methylarsonate), Tetramethylammonium–Sodium Double Salt. A solution of sodium