that the results of this study will provide a useful basis by which the magnetic properties of other mixed metal dimers may be characterized. Although such systems are still relatively rare, efforts to prepare and study heterogeneous magnetic dimers have been made in recent years.[14-18] It appears that mixed dimers may also occur in biological systems. Cytochrome oxidase is reported to contain an antiferromagnetically coupled iron(III)–copper(II) system.[19-21] It is interesting to note that a Fe(III)–Cu(II) dimer is isoelectronic with a Mn(II)–Cu(II) species. Unfortunately, the Fe(III)–Cu(II) system in cytochrome oxidase does not have an observable EPR signal. Presumably, this results from a very large zero-field splitting in the quintet ground state.[12]

Acknowledgment. The authors thank Professor Barry B. Garrett of Florida State University for the use of the E-12 EPR spectrometer and for many helpful discussions. This work was partially supported by National Science Foundation Grant CHE 77-12557.

Registry No. $[Cu(pyO)Cl_2 \cdot H_2O]_2$, 57428-25-8; Mn^{2+}, 16397-91-4.

Supplementary Material Available: A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Model Compounds for Copper(I) Sites in Hemocyanins: Synthesis, Structure, and Properties of Copper(I)–Histamine Complexes

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Received December 6, 1979

A methanolic suspension of CuI in the presence of histamine (hm) (hm/CuI > 2) reacts reversibly with carbon monoxide absorbing 1 mol of CO/mol of copper. The absorption of CO produces a slightly green solution from which, by addition of $NaBPh_4$, white crystals of $[Cu_2(hm)_3(CO)_2](BPh_4)_2$ (I) [ν_{CO}(Nujol) 2055 and 2066 cm^{-1}] have been obtained. The X-ray analysis performed on I showed the presence of the dimeric cation $[Cu_2(hm)_3(CO)_2]^{2+}$, with one histamine molecule chelated to each copper atom, one histamine bridging the two metal atoms, and a carbon monoxide molecule completing the pseudotetrahedral geometry around the metal. While the chelating histamine is a 4-imidazole derivative, the bridging one is present in the 5-imidazole form. The reaction between a methanolic suspension of CuCOCl with histamine, carried out at 0 °C, gave a solution from which, by addition of $NaBPh_4$, [Cu(hm)CO]BPh_4 (II) [ν_{CO}(Nujol) 2091 cm^{-1}] was recovered as a crystalline solid. II reacts with an excess of histamine, producing I. A polymeric structure is suggested for II, in which copper(I) is supposed to achieve the tetracoordination through an imidazole ring bridging two copper(I) atoms. Carbonylated solutions from which I and II are obtained react with cyclohexyl isocyanide losing CO and giving, on addition of $NaBPh_4$, the same complex $[Cu(hm)(C_6H_{11}NC)](BPh_4)$ [ν_{CN}(Nujol) 2180 cm^{-1}]. Crystallographic details for $[Cu_2(hm)_3(CO)_2](BPh_4)_2$: space group $P2_1$ (monoclinic), a = 15.901 (2) Å, b = 13.301 (2) Å, c = 14.826 (2) Å, β = 109.30 (1)°; Z = 2. The final R was 9.4% for 2894 observed reflections.

Introduction

The value of a "model compound" depends on the closeness of its physical parameters and chemical properties to those of biological or catalytically active systems. As concerns compounds containing a metal center, these parameters could be (i) the nature of the metal along with its oxidation state and d electron configuration, (ii) the coordination number and coordination geometry around the metal, and (iii) the donor atoms binding the metal active site, along with the nature of the organic molecule bearing these bonding groups. Moreover, the effectiveness of a "model compound" comes out from the degree to which it is able to imitate some of the key functions displayed by the living or catalytic systems.

The presence of copper(I) and copper(II) in some metalloproteins is very well documented.[1-3] While various model compounds have been found for imitating the Cu(II)–protein interaction,[4] very little information is available regarding copper(I) models for Cu(I)–protein interaction.[3,5] One reason for the limited amount of information available is that the oxidation state +1 for copper is mainly stabilized by π-bonding soft donor atoms, i.e., PR_3 and SR_2, which are absent in living systems. Amino groups and imidazolic nitrogens, which bind copper(I) in some metalloproteins, cause, under ordinary reaction conditions, the disproportionation of copper(I) to copper(II) and copper metal.

Rather recently, we found that the use of CuCOCl and CuI, as sources of copper(I) and polydentate amines in a carbon monoxide atmosphere, allows the isolation of mono- and di-

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nuclear copper(I) complexes.[6,7] We describe now the same reactions when polydentate amines have been replaced by histamine, which is supposed to be the basic unit binding copper(I) in hemocyanins.[1-3,5] This work, which was briefly communicated,[8] allowed the isolation of two interrelated copper(I)–histamine complexes bonding carbon monoxide and cyclohexyl isocyanide, as copper(I) does in hemocyanins.

Experimental Section

Reactions were carried out under an atmosphere of purified nitrogen. Methanol, tetrahydrofuran, and diethyl ether were dried and distilled before use. CuI and CuCl have been prepared as in the literature,[9] Cyclohexyl isocyanide was distilled before use. Infrared spectra were recorded with a Perkin-Elmer 282 spectrophotometer. The CO absorption and evolution were gas volumetrically measured.

Histamine Free Base. Histamine (hm) free base was prepared from the commercially available histamine dihydrochloride. Histamine dihydrochloride (9.8 g, 53.2 mmol) was dissolved in hot methanol (100 mL) and treated with a methanolic (100 mL) solution of CH_3ONa (106.5 mmol) obtained by reacting metallic sodium (2.45 g, 106.5 mmol) with CH_3OH (100 mL). The addition of Et_2O (250 mL) to the resulting solution precipitated all NaCl, which was filtered out. The solution evaporated to dryness gave a yellow syrup, which partially dissolved in $CHCl_3$ (200 mL). The undissolved solid was filtered out and the chloroform solution partially evaporated to give an oil which crystallized by the addition of some crystals of pure histamine.

Synthesis of $[Cu_2(hm)_3(CO)_2](BPh_4)_2$. CuI (2.10 g, 11.03 mmol), suspended in methanol (20 mL) containing histamine (2.90 g, 26.13 mmol), absorbed carbon monoxide, giving in 30 min a solution from which, by addition of $NaBPh_4$ (3.78 g, 11.05 mmol), $[Cu_2(hm)_3(CO)_2](BPh_4)_2$ (I) was obtained as a white or slightly green solid (ca. 50%). I, dried in vacuo, did not lose CO. It was stable in the solid state at room temperature for a long time under an N_2 atmosphere. Anal. Calcd for $[Cu_2(hm)_3(CO)_2](BPh_4)_2$ (I), $C_{65}H_{67}B_2Cu_2N_9O_2$: C, 67.61; H, 5.81; N, 10.92; Cu, 11.0. Found: C, 67.16; H, 5.89; N, 10.38; Cu, 10.59. I reacted with a methanolic solution of $P(OEt)_3$, released 0.9 mol of CO/mol of Cu. In vacuo the carbonylated solution lost carbon monoxide giving a white solid, with a very high content of CuI, whose nature was not possible to ascertain.

Synthesis of [Cu(hm)CO](BPh$_4$). The slow addition of histamine (1.17 g, 10.54 mmol), dissolved in methanol (20 mL), to a suspension of CuCOCl (10.50 mmol), cooled at 0°C, induced the complete dissolution of the solid. In vacuo this solution lost carbon monoxide and gave a white solid, which dissolved again in the presence of CO. By addition of $NaBPh_4$ (3.60 g, 10.53 mmol) dissolved in methanol (20 mL), [Cu(hm)CO](BPh_4) was obtained as a white crystalline solid. Anal. Calcd for [Cu(hm)CO](BPh_4) (II), $C_{30}H_{29}BCuN_3O$: C, 69.06; H, 5.56; N, 8.06; Cu, 12.18. Found: C, 67.94; H, 5.47; N, 7.99; Cu, 12.16. II lost CO in vacuo neither when it was in the solid state nor when it was suspended in CH_3OH. Carbon monoxide was displaced in II by $P(OEt)_3$, giving 0.95 mol of CO/mol of Cu. [Cu(hm)CO](BPh_4) reacted with an excess of histamine in methanol giving a solution from which $[Cu_2(hm)_3(CO)_2](BPh_4)_2$ was recovered by concentration in a stream of carbon monoxide.

Carbonylation of CuI with a hm/Cu Molar Ratio Lower Than 1. CuI (2.5 g, 13.12 mmol), suspended in CH_3OH (20 mL) containing histamine (1.30 g, 11.71 mmol), absorbed CO for 20 min. The unreacted CuI was filtered out, while, by addition of $NaBPh_4$ to the resulting solution, a white solid was obtained (1.1 g) displaying three CO bands (Nujol) at 2091, 2066, and 2055 cm^{-1}. The last two have the same intensity, while the first one is by far the most intense.

Synthesis of [Cu(hm)($C_6H_{11}NC$)](BPh_4). Method A. Carbon monoxide was absorbed by a suspension of CuCl (1.04 g, 10.51 mmol) in methanol (30 mL) at room temperature and atmospheric pressure. To this suspension cooled at −20 °C was added dropwise a solution of histamine (2.33 g, 21.0 mmol) in methanol (20 mL). The final solution reacted with neat $C_6H_{11}NC$ (2.3 mL, 21.91 mmol) to lose carbon monoxide. The further addition of $NaBPh_4$ (3.70 g, 10.82 mmol) dissolved in methanol (20 mL) gave an oil which solidified on stirring. This solid was partially soluble in THF (30 mL). The undissolved solid was filtered out, while the solution, evaporated to dryness, gave an oil which collected with Et_2O (20 mL) and THF (5 mL) produced a white microcrystalline solid (2.0 g) [ν_{CN}(Nujol) 2180 cm^{-1}]. Anal. Calcd for [Cu(hm)($C_6H_{11}NC$)](BPh_4) (III), $C_{36}H_{40}BCuN_4$: C, 71.72; H, 6.64; N, 9.30; Cu, 10.55. Found: C, 71.92; H, 7.09; N, 9.35; Cu, 10.04.

Method B. Carbon monoxide was absorbed by a suspension of CuI (1.73 g, 9.11 mmol) in a methanolic (30 mL) solution of histamine (2.74 g, 24.7 mmol). Some undissolved solid was filtered out. The addition of cyclohexyl isocyanide (2.0 mL, 19.0 mmol) to this solution caused the loss of CO. When $NaBPh_4$ (3.20 g, 9.11 mmol) dissolved in methanol (20 ml) was added, a white microcrystalline solid was obtained (2.7 g). Anal. Calcd for [Cu(hm)($C_6H_{11}NC$)](BPh_4) (III), $C_{36}H_{40}BCuN_4$: C, 71.72; H, 6.64; N, 9.29; Cu, 10.54. Found: C, 71.39; H, 6.63; N, 9.29; Cu, 10.20.

X-ray Data for $[Cu_2(hm)_3(CO)_2](BPh_4)_2$. $C_{65}H_{67}B_2Cu_2N_9O_2$: M_r = 1155.0, monoclinic, a = 15.901 (2) Å, b = 13.301 (2) Å, c = 14.826 (2) Å, β = 109.30 (1)°, V = 2959 Å^3, Z = 2, D_c = 1.296 g cm^{-3}, $F(000)$ = 1208, space group $P2_1$ (from systematic absences and structural analysis), Cu Kα radiation, Ni filter, λ = 1.541 78 Å, μ = 12.5 cm^{-1}. Cell dimensions were determined from rotation and Weissenberg photographs; the values quoted were obtained from least-squares refinement of the θ angles of 30 reflections ($\theta > 31°$).

Data Collection. A thin plate of dimensions 0.06 × 0.32 × 0.40 mm, sealed in a glass capillary under nitrogen atmosphere, was mounted on a Siemens AED automated diffractometer. Intensity data were collected by using Ni-filtered Cu Kα radiation (λ = 1.541 78 Å) at take-off angle of 6°. The pulse-height discriminator was set to accept 90% of the Cu Kα peak. The moving-counter–moving-crystal scan technique was employed with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min). A standard reflection monitored every 20 reflections showed no systematic variation of intensity during data collection. For measuring intensity and background the "five-point technique"[10] was used. A total 4595 independent reflections were measured in the interval $6° < 2\theta < 120°$; 2894 of these, having $I > 2\sigma(I)$, were considered observed and used in the analysis. Lorentz and polarization corrections were applied in the usual way, no absorption correction was made (μr = 0.1).

Structure Determination and Refinement. The structure was solved by direct methods of phase determination with the program MULTAN,[11] assuming the centrosymmetric $P2_1/n$ space group. An E map computed by use of thee signs of 350 reflections with $|E| > 1.59$ revealed the positions of 34 nonhydrogen atoms. A successive Fourier synthesis computed with the contribution of these atoms showed the presence of a imidazole residue coordinated to copper but was inconsistent with its centrosymmetrical image. The $P2_1$ space group was then chosen, according to the presence of a few $h0l$ reflections with $h + l$ odd. Successive structure factors and Fourier calculations revealed a histamine molecule bridging between two independent copper atoms. The structure was refined in the $P2_1$ space group by a full-matrix least-squares program first isotropically to R = 13.8% and then anisotropically, for copper atoms only, down to R = 9.4%. The high correlations between pseudocentrosymmetrical atom parameters did not allow a better fit. Throughout the refinement, the phenyl rings were considered as rigid groups, each as a regular hexagon of carbon atoms having a fixed C–C bond length of 1.395 Å. Thus it was only necessary to further refine the locations and orientations of the eight pivot atoms within their ring. The B–C distances were constrained to be 1.70 Å. Fifty of the 67 hydrogen atoms were located in a difference Fourier map; the remaining atoms were introduced in their geometrically calculated positions. All the hydrogen atoms were refined in the last cycle of the refinement. A final ΔF map showed no peaks above the general background.

The function minimized was $\sum w|\Delta F|^2$ first with unit weights and then with $w = 2.9109/[\sigma^2(F_o) + 0.002F_o^2]$. No evidence for secondary extinction was found.

Complex scattering factors were used during refinement. Atomic scattering factors used throughout the calculations were taken from

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Table I. Final Nonhydrogen Atomic Fractional Coordinates (×10⁴) with Estimated Standard Deviations in Parentheses

	x/a	y/b	z/c		x/a	y/b	z/c
Cu(1)	1344 (2)	2570 (4)	9021 (2)	C(34)	2749 (4)	5244 (4)	1330 (4)
Cu(2)	3706 (2)	7415 (3)	6158 (2)	C(35)	3439 (4)	5707 (4)	1099 (4)
C	499 (16)	1981 (19)	8035 (16)	C(36)	3298 (4)	6635 (4)	636 (4)
O	−57 (14)	1533 (18)	7529 (15)	C(41)	3326 (4)	8788 (5)	58 (5)
C*	4593 (13)	8082 (15)	7019 (13)	C(42)	3632 (4)	9481 (5)	801 (5)
O*	5184 (11)	8530 (14)	7472 (11)	C(43)	4464 (4)	9932 (5)	987 (5)
C(1)	1861 (9)	2550 (12)	11186 (8)	C(44)	4991 (4)	9690 (5)	430 (5)
C(2)	1564 (10)	2777 (12)	11902 (10)	C(45)	4686 (4)	8996 (5)	−313 (5)
N(3)	721 (9)	3125 (11)	11465 (9)	C(46)	3854 (4)	8545 (5)	−498 (5)
C(4)	529 (9)	3104 (11)	10541 (9)	C(51)	1775 (4)	8093 (5)	−1315 (4)
N(5)	1219 (7)	2764 (9)	10311 (7)	C(52)	1832 (4)	8860 (5)	−1933 (4)
C(6)	2720 (10)	2063 (12)	11258 (10)	C(53)	1335 (4)	8804 (5)	−2903 (4)
C(7)	3110 (11)	2330 (14)	10509 (11)	C(54)	779 (4)	7981 (5)	−3254 (4)
N(8)	2614 (9)	2006 (11)	9568 (9)	C(55)	722 (4)	7214 (5)	−2636 (4)
C(1*)	3162 (9)	7313 (11)	3988 (8)	C(56)	1219 (4)	7270 (5)	−1666 (4)
C(2*)	3476 (10)	7013 (12)	3282 (9)	B*	2676 (3)	1605 (4)	5202 (3)
N(3*)	4316 (8)	6639 (9)	3737 (7)	C(21*)	3286 (4)	839 (5)	4736 (4)
C(4*)	4465 (9)	6683 (11)	4671 (9)	C(22*)	3196 (4)	890 (5)	3769 (4)
N(5*)	3800 (7)	7119 (9)	4869 (7)	C(23*)	3691 (4)	248 (5)	3395 (4)
C(6*)	2303 (10)	7827 (12)	3904 (9)	C(24*)	4276 (4)	−445 (5)	3987 (4)
C(7*)	1904 (10)	7615 (14)	4691 (10)	C(25*)	4365 (4)	−496 (5)	4955 (4)
N(8*)	2440 (9)	8080 (11)	5582 (9)	C(26*)	3870 (4)	146 (5)	5329 (4)
C(11)	2623 (13)	5059 (16)	7253 (14)	C(31*)	1663 (4)	1065 (5)	5014 (5)
C(12)	2893 (12)	5974 (14)	7327 (12)	C(32*)	1335 (4)	349 (5)	4296 (5)
N(13)	3295 (8)	6171 (11)	6597 (9)	C(33*)	490 (4)	−63 (5)	4126 (5)
C(14)	3332 (11)	5356 (14)	6081 (11)	C(34*)	−28 (4)	242 (5)	4674 (5)
N(15)	2870 (11)	4671 (13)	6517 (11)	C(35*)	299 (4)	957 (5)	5392 (5)
C(16)	2046 (15)	4418 (16)	7678 (12)	C(36*)	1144 (4)	1369 (5)	5563 (5)
C(17)	2259 (14)	4822 (16)	8636 (12)	C(41*)	3224 (4)	1706 (5)	6397 (4)
N(18)	1585 (12)	4248 (15)	8932 (12)	C(42*)	3093 (4)	981 (5)	7017 (4)
B	2327 (3)	8235 (4)	−136 (3)	C(43*)	3598 (4)	1009 (5)	7986 (4)
C(21)	1712 (4)	8975 (5)	329 (4)	C(44*)	4234 (4)	1761 (5)	8334 (4)
C(22)	1774 (4)	8859 (5)	1284 (4)	C(45*)	4365 (4)	2486 (5)	7714 (4)
C(23)	1275 (4)	9476 (5)	1677 (4)	C(46*)	3860 (4)	2459 (5)	6745 (4)
C(24)	715 (4)	10208 (5)	1115 (4)	C(51*)	2510 (4)	2742 (4)	4645 (4)
C(25)	653 (4)	10324 (5)	160 (4)	C(52*)	1685 (4)	3222 (4)	4405 (4)
C(26)	1152 (4)	9708 (5)	−233 (4)	C(53*)	1561 (4)	4155 (4)	3951 (4)
C(31)	2468 (4)	7102 (4)	403 (4)	C(54*)	2263 (4)	4608 (4)	3735 (4)
C(32)	1778 (4)	6640 (4)	634 (4)	C(55*)	3088 (4)	4128 (4)	3974 (4)
C(33)	1919 (4)	5711 (4)	1098 (4)	C(56*)	3211 (4)	3195 (4)	4429 (4)

ref 12 for Cu, from ref 13 for C, N, and O, and from ref 14 for hydrogen. All the calculations were made on a CYBER 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale (Bologna) using the SHELX-76 system of computer programs.[15]

The final positions for atoms are in Tables I and II. Observed and calculated structure factors together with the thermal parameters are listed in the supplementary material. Bond distances and angles and the equation of molecular planes are given in Tables III and IV.

Results

A general synthetic method for copper(I) carbonyls utilizes CuI and CuCOCl in methanol containing a polydentate amine such as ethylenediamine and diethylenetriamine, in a carbon monoxide atmosphere.[6,7] These amines can be replaced by histamine in the same reaction.[8]

A suspension of CuI in methanol containing histamine free base, hm, absorbs carbon monoxide reversibly at room temperature and atmospheric pressure, giving a slightly green solution [ν_{CO} = 2070 cm^{-1}] which loses CO in vacuo. Upon removal of CO from this solution, a white solid was obtained, which was shown to be mainly the starting CuI. The addition of $NaBPh_4$ to the carbonylated solution, when the histamine/Cu molar ratio is higher than 2, gave $[Cu_2(hm)_3(CO)_2](BPh_4)_2$ (I). While the solution is very reactive with oxygen and moisture, I is stable in the solid state and it displays two close CO stretching vibrations at 2055 and 2066 cm^{-1}.

$$2CuI + 3hm + 2CO \xrightarrow[-NaI]{NaBPh_4} \underset{I}{[Cu_2(hm)_3(CO)_2](BPh_4)_2} \quad (1)$$

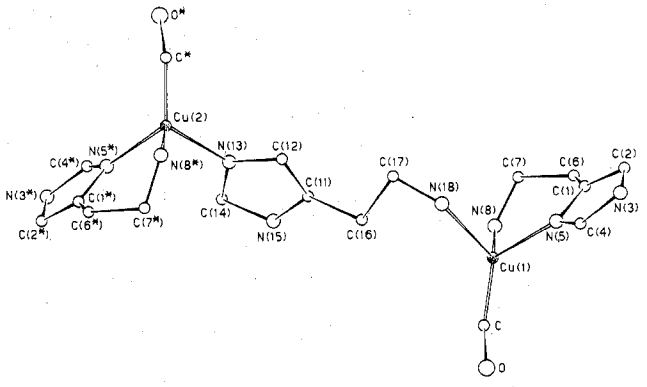

Figure 1. Molecular structure of $[Cu_2(hm)_3(CO)_2]^{2+}$.

Solid-State Structure of $[Cu_2(hm)_3(CO)_2](BPh_4)_2$. The crystals of complex I are formed by the cation $[Cu_2(hm)_3(CO)_2]^{2+}$ and the tetraphenylborate anion, BPh^-_4. A drawing of the dinuclear cation is shown in Figure 1, while the more relevant bond distances and angles are presented in Table III. The two copper atoms, sited in pseudotetrahedral geometries, are bridged by a histamine molecule. The coordination sphere

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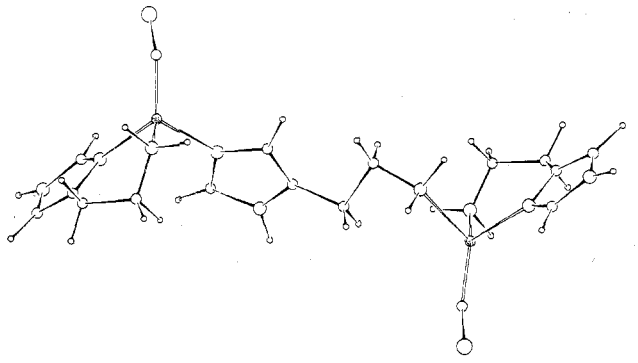
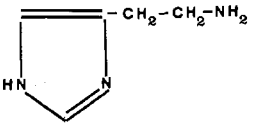
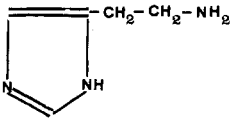


Figure 2. A drawing of the pseudocentrosymmetric cation $[Cu_2(hm)_3(CO)_2]^{2+}$ showing hydrogen atoms.

around each copper is completed by a chelating histamine and a carbon monoxide group. Histamine is present in the macro cation in the 4-(2-aminoethyl)imidazole form acting as chelating ligand and in the 5-(2-aminoethyl)imidazole[16] form



4-(2-aminoethyl)-imidazole



5-(2-aminoethyl)-imidazole

acting as bridging ligand, as can be deduced from Figure 2 showing the hydrogen atoms. Bridging histamine binds Cu(1) with the amino group and Cu(2) with the imidazolic nitrogen N(13). It exhibits the extended trans configuration of the alkyl chain, the torsion angle C(11)–C(16)–C(17)–N(18) being −173°. The imidazole ring is planar within the limits of accuracy; the dihedral angle between its mean plane and the plane of the aminoethyl group is 33.4°, a value significantly different from that observed in the two chelating histamine molecules. Bond distances and angles in the chelating histamine ligands are in good behavior.[17] The imidazole groups are planar; the dihedral angles between this plane and the plane of the aminoethyl group are 51.7 and 57.2° for the ligand chelated to Cu(1) and Cu(2), respectively. The geometries of the imidazole rings seem not to be affected by coordination. Differences in bond distances and angles between chelating and bridging histamine molecules are of little significance. The further structural interest depends on the values associated with the CuCO unit. Cu–C, C–O, and Cu–C–O bond distances and angles (Table III) agree well with the values reported for the other few copper carbonyl complexes known.[6,7,18,19]

The nonequivalence of the coordination environment around Cu(1) and Cu(2) in the pseudocentrosymmetric dinuclear cation is shown by two sharp IR CO bands (Nujol) of the same intensity at 2055 and 2066 cm^{-1}. These values are unusually low for copper carbonyls and very close to that found for carboxyhemocyanin [2063 cm^{-1}].[20]

Carrying out reaction 1 with a CuI/histamine molar ratio lower than 1 led to only a partial dissolution of the copper salt. The filtered solution, which showed a broad single CO band at 2070 cm^{-1}, gave, on addition of $NaBPh_4$, a solid displaying

Table II. Fractional Coordinates (×10⁴) of H Atoms

	x/a	y/b	z/c
H(2)	1903 (25)	2694 (25)	12689 (25)
H(3)	262 (25)	3399 (25)	11807 (25)
H(4)	−103 (25)	3339 (25)	10026 (25)
H(61)	3214 (25)	2172 (25)	11983 (25)
H(62)	2605 (25)	1195 (25)	11260 (25)
H(71)	3799 (25)	1954 (25)	10679 (25)
H(72)	3165 (25)	3090 (25)	10454 (25)
H(81)	3001 (25)	2142 (25)	9082 (25)
H(82)	2573 (25)	1141 (25)	9558 (25)
H(2*)	3130 (25)	7092 (25)	2526 (25)
H(3*)	4767 (25)	6356 (25)	3370 (25)
H(4*)	5093 (25)	6398 (25)	5230 (25)
H(6*1)	2370 (25)	8597 (25)	3871 (25)
H(6*2)	1802 (24)	7583 (25)	3212 (24)
H(7*1)	1958 (25)	6728 (25)	4804 (25)
H(7*2)	1211 (25)	7741 (25)	4482 (25)
H(8*1)	2514 (25)	8864 (25)	5434 (25)
H(8*2)	2102 (25)	8046 (25)	6114 (25)
H(12)	2838 (25)	6540 (25)	7893 (25)
H(14)	3626 (25)	5244 (25)	5522 (25)
H(15)	2773 (25)	3865 (26)	6271 (25)
H(161)	2156 (25)	3678 (25)	7698 (25)
H(162)	1347 (25)	4624 (26)	7377 (25)
H(171)	2955 (25)	4496 (25)	9008 (25)
H(172)	2283 (25)	5589 (26)	8670 (25)
H(181)	964 (25)	4545 (26)	8425 (25)
H(182)	1670 (25)	4546 (26)	9638 (25)
H(22)	2225 (24)	8279 (25)	1747 (24)
H(23)	1344 (24)	9374 (24)	2443 (24)
H(24)	341 (24)	10661 (24)	1423 (24)
H(25)	214 (24)	10856 (24)	−268 (24)
H(26)	1125 (24)	9758 (24)	−953 (24)
H(32)	1140 (24)	6978 (24)	462 (24)
H(33)	1395 (24)	5331 (24)	1272 (24)
H(34)	2869 (24)	4490 (24)	1696 (24)
H(35)	4092 (24)	5314 (24)	1284 (24)
H(36)	3841 (24)	6963 (24)	451 (24)
H(42)	3233 (24)	9673 (25)	1229 (24)
H(43)	4709 (24)	10443 (25)	1551 (24)
H(44)	5645 (24)	10002 (25)	562 (24)
H(45)	5082 (24)	8747 (25)	−753 (24)
H(46)	3611 (24)	7966 (24)	−1070 (24)
H(52)	2239 (24)	9495 (24)	−1681 (24)
H(53)	1382 (24)	9372 (24)	−3401 (24)
H(54)	400 (24)	7914 (25)	−4008 (24)
H(55)	297 (24)	6563 (25)	−2908 (24)
H(56)	1156 (24)	6685 (24)	−1179 (24)
H(22*)	2768 (24)	1410 (24)	3340 (24)
H(23*)	3635 (24)	276 (24)	2665 (24)
H(24*)	4649 (24)	−961 (24)	3692 (24)
H(25*)	4820 (24)	−1073 (24)	5411 (24)
H(26*)	3957 (24)	61 (24)	6072 (24)
H(32*)	1738 (24)	112 (24)	3858 (24)
H(33*)	241 (24)	−635 (24)	3533 (24)
H(34*)	−693 (24)	−128 (24)	4517 (24)
H(35*)	−110 (24)	1140 (24)	5810 (24)
H(36*)	1391 (24)	1884 (24)	6132 (24)
H(42*)	2572 (24)	393 (24)	6763 (24)
H(43*)	3509 (24)	426 (24)	8458 (24)
H(44*)	4628 (24)	1752 (24)	9069 (24)
H(45*)	4852 (24)	3061 (24)	7990 (24)
H(46*)	3682 (24)	3011 (24)	6242 (24)
H(52*)	1151 (24)	2853 (24)	4567 (24)
H(53*)	919 (24)	4507 (24)	3767 (24)
H(54*)	2162 (24)	5300 (24)	3386 (24)
H(55*)	3628 (24)	4444 (24)	3804 (24)
H(56*)	3837 (24)	2794 (24)	4608 (24)

three carbonyl bands at 2055, 2066, and 2091 cm^{-1}. While the first two belong to I, the band at 2091 suggests the presence of a second carbonyl complex, II. The synthesis of II, which should involve a lower histamine/copper ratio, was achieved by the route

$$CuCOCl + hm \xrightarrow[CO,\ 0\ °C,\ -NaCl]{NaBPh_4} \underset{II}{[Cu(hm)CO](BPh_4)} \qquad (2)$$

(16) Bonnet, J. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4829.
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(20) Alben, J. O.; Yen, L.; Farrier, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 4475.

Table III. Bond Distances (Å) and Angles (Deg) in the $[Cu_2(hm)_3(CO)_2]^{2+}$ Cation

Coordination Sphere			
Cu(1)-C	1.80 (2)	Cu(2)-C*	1.79 (2)
Cu(1)-N(5)	2.00 (1)	Cu(2)-N(5*)	2.00 (1)
Cu(1)-N(8)	2.05 (2)	Cu(2)-N(8*)	2.10 (2)
Cu(1)-N(18)	2.28 (2)	Cu(2)-N(13)	1.97 (1)
C-Cu(1)-N(5)	123.2 (9)	C*-Cu(2)-N(5*)	119.1 (8)
C-Cu(1)-N(8)	122.2 (9)	C*-Cu(2)-N(8*)	120.2 (8)
C-Cu(1)-N(18)	118.3 (9)	C*-Cu(2)-N(13)	116.7 (7)
N(5)-Cu(1)-N(8)	93.7 (5)	N(5*)-Cu(2)-N(8*)	93.3 (5)
N(5)-Cu(1)-N(18)	90.0 (6)	N(5*)-Cu(2)-N(13)	106.7 (5)
		N(8*)-Cu(2)-N(13)	96.3 (6)
N(8)-Cu(1)-N(18)	102.6 (7)	Cu(2)-N(5*)-C(1*)	126.8 (9)
Cu(1)-N(5)-C(1)	126.2 (9)	Cu(2)-N(5*)-C(4*)	128.0 (9)
Cu(1)-N(5)-C(4)	129.7 (9)	Cu(2)-N(8*)-C(7*)	112.7 (11)
Cu(1)-N(8)-C(7)	115.5 (11)	Cu(2)-N(13)-C(14)	114.2 (11)
Cu(1)-N(18)-C(17)	132.0 (14)	Cu(2)-N(13)-C(12)	132.5 (12)
Carbonyl Ligand			
C-O	1.12 (3)	Cu(1)-C-O	169 (2)
C*-O*	1.13 (3)	Cu(2)-C*-O*	172 (2)
Histamine Ligand			
C(1)-C(2)	1.33 (2)	N(5)-C(1)	1.39 (2)
C(2)-N(3)	1.36 (2)	C(1)-C(6)	1.48 (2)
N(3)-C(4)	1.30 (2)	C(6)-C(7)	1.48 (2)
C(4)-N(5)	1.33 (2)	C(7)-N(8)	1.42 (2)
C(1*)-C(2*)	1.36 (2)	N(5*)-C(1*)	1.39 (2)
C(2*)-N(3*)	1.37 (2)	C(1*)-C(6*)	1.49 (2)
N(3*)-C(4*)	1.33 (2)	C(6*)-C(7*)	1.53 (2)
C(4*)-N(5*)	1.32 (2)	C(7*)-N(8*)	1.45 (2)
C(11)-C(12)	1.28 (3)	N(15)-C(11)	1.38 (3)
C(12)-N(13)	1.45 (2)	C(11)-C(16)	1.53 (3)
N(13)-C(14)	1.34 (2)	C(16)-C(17)	1.45 (2)
C(14)-N(15)	1.45 (3)	C(17)-N(18)	1.49 (3)
N(5)-C(1)-C(2)	111 (1)	N(5*)-C(1*)-C(2*)	109 (1)
N(5)-C(1)-C(6)	122 (1)	N(5*)-C(1*)-C(6*)	122 (1)
C(2)-C(1)-C(6)	127 (1)	C(2*)-C(1*)-C(6*)	129 (1)
C(1)-C(2)-N(3)	104 (1)	C(1*)-C(2*)-N(3*)	106 (1)
C(2)-N(3)-C(4)	110 (1)	C(2*)-N(3*)-C(4*)	108 (1)
N(3)-C(4)-N(5)	110 (1)	N(3*)-C(4*)-N(5*)	112 (1)
C(4)-N(5)-C(1)	104 (1)	C(4*)-N(5*)-C(1*)	105 (1)
C(1)-C(6)-C(7)	116 (1)	C(1*)-C(6*)-C(7*)	117 (1)
C(6)-C(7)-N(8)	115 (1)	C(6*)-C(7*)-N(8*)	110 (1)
N(15)-C(11)-C(12)	104 (2)	C(12)-N(13)-C(14)	113 (1)
N(15)-C(11)-C(16)	119 (2)	N(13)-C(14)-N(15)	98 (1)
C(12)-C(11)-C(16)	136 (2)	C(14)-N(15)-C(11)	116 (2)
C(11)-C(12)-N(13)	109 (2)	C(11)-C(16)-C(17)	103 (2)
C(16)-C(17)-N(18)	98 (2)		

CuCl in methanol absorbs at 0 °C carbon monoxide, producing a white crystalline unisolable solid which is the so-called "CuCOCl".[21] This compound reacted readily with histamine at 0 °C, under an atmosphere of CO, producing a solution from which II crystallized out on addition of $NaBPh_4$. The carbonylated solution lost carbon monoxide in vacuo, giving a solid which was mainly the starting CuCl. Therefore, the loss of CO occurs simultaneously with the loss of the ancillary ligand by copper(I).

II displays a CO stretching band at 2091 cm^{-1}. As expected on the basis of the results outlined above, II, suspended in methanol containing histamine and in a carbon monoxide atmosphere, is converted to I (see Experimental Section). Any attempt to produce a more histamine-rich copper(I) complex failed, in spite of the successfull isolation of an ethylenediamine complex of the following stoichiometry: $[Cu(en)_2(CO)]I$.[7]

The carbonylated solutions from which I and II were obtained lose CO upon reacting with an excess of $C_6H_{11}NC$. The addition of $NaBPh_4$ to this solution produced $[Cu(hm)(C_6H_{11}NC)](BPh_4)$ (III) as a white crystalline solid, with a single strong CN band at 2180 cm^{-1}. In spite of the presence of an excess of both histamine and $C_6H_{11}NC$, III contains one histamine and one isocyanide group per copper.

(21) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191.

Table IV. Equations of Least-Squares Planes and, in Brackets, Distances (Å) from These Planes[a]

Plane 1: Imidazole ring C(1), C(2), N(3), C(4), N(5)

$-0.3656X - 0.9303Y - 0.0296Z = -2.7031$

[C(1) 0.006, C(2) −0.003, N(3) −0.004, C(4) 0.006, N(5) −0.006, C(6) 0.120]

Plane 2: Aminoethyl Group C(6), C(7), C(8)

$-0.4818X + 0.8612Y - 0.1620Z = 0.3853$

Plane 3: Imidazole Ring C(1*), C(2*), N(3*), C(4*), N(5*)

$-0.4244X - 0.9055Y - 0.0021Z = -10.1257$

[C(1*) 0.002, C(2*) 0.007, N(3*) −0.016, C(4*) 0.022, N(5*) −0.014, C(6*) −0.054]

Plane 4: Aminoethyl Group C(6*), C(7*), N(8*)

$-0.4967X + 0.8320Y - 0.2471Z = 6.4428$

Plane 5: Imidazole Ring C(11), C(12), N(13), C(14), N(15)

$-0.7080X + 0.2638Y - 0.6551Z = -5.3184$

[C(11) 0.008, C(12) −0.017, N(13) 0.015, C(14) −0.018, N(15) 0.013, C(16) 0.190]

Plane 6: Aminoethyl Group C(16), C(17), N(18)

$-0.5805X + 0.7347Y - 0.3511Z = 0.8404$

[a] The transformation matrix from monoclinic x, y, and z to orthogonal X, Y, and Z is

$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}$$

Discussion

Reactions 1 and 2 represent novel and general synthetic routes to copper(I) complexes. Notwithstanding that copper(I) chemistry is dominated by the disproportionation of copper(I) to copper(II) and copper metal,[22] this reaction does not occur under the conditions specified for reactions 1 and 2. The presence of I^- and/or CO as reducing agents and the use of methanol as reaction solvent may play an important role. Moreover we found that the donor atoms providing the best Cu–CO bond stabilization are amino groups and, as expected, the density of the ligand further increases this stability. A further stabilization is observed when these complexes are isolated as tetraphenylborate derivatives.

Model Compounds. The knowledge of (a) the synthetic routes to Cu(I)–CO systems, (b) the factors affecting both the +1 oxidation state and Cu–CO bonding formation, and (c) the functional groups binding Cu(I) or being competitive with CO will contribute to the discovery of the rules which govern the interaction between copper(I) and naturally occurring ligands. In fact, the copper binding sites, the number and the nature of the ligands, and their geometry are the salient questions still to be answered.

It is very well-known that both copper(I) and copper(II) occur in couple in some metalloproteins.[1-3] While a rich harvest of information is available for copper(II) sites, the opposite situation is found for copper(I).[3] As possible functional groups binding copper(I) in hemocyanins, imidazole groups of histamine, amino groups, and disulfide bridges have been considered. Deoxygenated hemocyanins contain copper(I), as shown by the easy reconstitution with copper(I)–acetonitrile complex.[1] Moreover, hemocyanins yield reversibly a colorless compound with CO and in some cases with EtNC.

(22) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115.

These characteristics of hemocyanins can be usefully compared with some features of the copper(I)–histamine system: the reversible absorption of 1 mol of CO/mol of Cu; the loss of CO causing the copper–histamine bonding breaking; the high stabilization of +1 oxidation state for copper(I); the isolation in the solid state of the two copper(I)–histamine complexes, I and II; and the rather low CO stretching frequencies in complex II [ν_{CO} 2055, 2066 cm^{-1}]. The isolation of complexes I and II shows that at least two interrelated copper(I) sites can be active in binding carbon monoxide. Their genesis and nature will be discussed below.

On the basis of the experimental data presented in the preceding section, the reaction of copper(I), CuI or CuCOCl, and histamine in the presence of carbon monoxide can be accommodated by the scheme

$$Cu^+ + hm + CO \overset{S}{\rightleftharpoons} \underset{A}{[Cu(hm)(CO)S]^+}$$

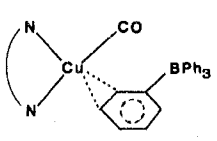
S = solvent

A species like A, in which copper(I) achieves the tetracoordination in solution with a solvent molecule (S), is probably the common precursor for complexes I and II, isolated in the solid state. The rather low CO stretching frequency (2070 cm^{-1}) of the solution is on behalf of the tetracoordination around copper(I). Moreover, the same CO band appearing when CO is absorbed by CuI in the presence of either an excess or a default of histamine supports the presence in solution of the same precursor for both cases. The origin of I from A can be described as involving the substitution of the S molecule by the free histamine present in solution (reaction 1) when $NaBPh_4$ causes the precipitation of the cation. With lack of an excess of histamine (reaction 2), this substitution can be realized by the NH group of another molecule. This corresponds to a polymerization process of the $[Cu(hm)CO]^+$ unit with the imidazole bridging two coppers(I), as depicted in the proposed structure of complex II (vide infra).

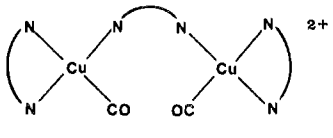
Coordination Environment of Copper(I) in Histamino Complexes. The solid-state structure of $[Cu_2(hm)_3(CO)_2](BPh_4)_2$ (I) is the reference for discussing the structure of the "model compounds" here reported.

While copper(I) displays a rather wide range of coordination numbers, the tetracoordination here found is commonly encountered in amine–carbonyl complexes.[6,7] Higher coordination numbers must be taken into account for special forced interaction.[19,23] It is notable that histamine is found in the two possible tautomeric forms and it displays the two claimed bonding modes with a metal.[24] Free histamine or bidentate histamine chelated to a metal was found always in the 4-(2-aminoethyl)imidazole form, as we found in complex I,[17] while the bridging histamine is present as 5-(2-aminoethyl)imidazole. Only the first form exhibits the very well-known biological activity.[16] The structural parameters associated with the Cu-chelating histamine do not differ significantly from those reported for the $[Cu(hm)_2]^{2+}$ complexes,[17] no data being available for other Cu(I)–histamine or histamine-like complexes. Special attention should be deserved to the bonding mode of the bridging histamine in complex I. Copper(I) is bound to the N(3) of the imidazole ring, whereas in histidine and histidyl peptide chelates, the imidazole N(1) atom is invariably involved. In fact, the simulation of the metal–protein interactions by simpler systems is made difficult for the fact that histidine and histidyl peptides have a great tendency to act as chelating ligands.[24] The only complex in which an imidazole side chain has been shown to act in a nonchelating fashion is the copper–carnosine complex.[25] The nonequivalence of the coordination environment around Cu(1) and Cu(2), in the pseudocentrosymmetric cation is shown by the two close CO stretching frequencies with the same intensity at 2055 and 2066 cm^{-1}. This frequency compares very well with that found for carboxyhemocyanin (2063 cm^{-1}).[20] The relative arrangement as well as the distance between the metal centers prevents their interaction with the same substrate to be activated.[26]

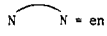
Suggestions concerning the structure of II, lacking an X-ray analysis, come both from the Cu–en–CO chemistry[7] and from the structure of I. The overall structures of I and of $[Cu_2(en)_3(CO)_2]^{2+}$ are rather similar in terms of coordination geometry around the metal and of the two bonding modes showed by hm and en, respectively. In $[Cu(en)(CO)(BPh_4)]$,



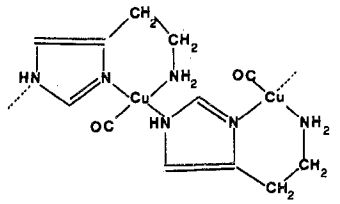
A sketch of the structure of $[Cu(en)(CO)(BPh_4)]$



A sketch of the structure of $[Cu_2(en)_3(CO)_2]^{2+}$



which resembles II, copper achieves the tetracoordination with a bidentate en and carbon monoxide and a long range interaction with a C–C unit of a phenyl group of the BPh_4 anion. Due to the high tendency of copper(I) in these complexes to achieve the tetracoordination, we feel that the open site around copper(I) in both $[Cu(en)CO]^+$ and II is probably filled in solution by a molecule of solvent (see species A). This is suggested both from the solid-state structure of $[Cu(en)(CO)(BPh_4)]$ and from the fact that the CO frequency in solution (2070 cm^{-1}) falls in the range expected for a more basic tetracoordinated copper(I). However, while the only possibility for $[Cu(en)(CO)]^+$ to achieve the tetracoordination in the solid state is the contact interaction even with the poor coordinating anion BPh_4^-, for complex II an NH group is further available on the imidazole ring of another molecule. The significant difference in CO stretching frequency between $[Cu(en)(CO)(BPh_4)]$ and II (2117 vs. 2091 cm^{-1}) suggests the presence in II of a fourth ligand around copper(I), more basic than a C=C bond. Therefore we suggest a polymeric structure for II with imidazole bridging two metal atoms. In



The proposed polymeric structure for $[Cu(fun)(CO)]^+$

fact, the high flexibility in metal–imidazole bonding would allow this kind of interaction.[27] A further support for the existence of this rather strong intermolecular Cu(I)–imidazole interaction appearing in the solid state would come from the stoichiometry of complex III. While carbonylated solutions of copper(I) in the presence of en or tmen react with $C_6H_{11}NC$, giving the corresponding diisocyanide complexes, [Cu-

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(25) Freeman, H. C.; Szymanski, J. T. *Acta Crystallogr.* **1967**, *22*, 406.
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$(en)(C_6H_{11}NC)_2]^+$ and $[Cu(tmen)(C_6H_{11}NC)_2]^+$,[28] carbonylated solutions of copper(I)–histamine allowed the isolation of $[Cu(hm)(C_6H_{11}NC)](BPh_4)$ only. This suggests that the NH group of an adjacent complex would compete either with the solvent or with a basic isocyanide. Therefore histamine provides, at least in the solid state, three different nitrogens for each copper, which may require in all these complexes a tetracoordination. On this basis, a polymeric structure for $[Cu(hm)(C_6H_{11}NC)]^+$ is suggested as for II, in which histamine shows the third bonding mode observed in these complexes.

Acknowledgment. We thank the CNR (Rome) for financial support.

Registry No. I, 73953-05-6; II, 73940-68-8; III, 73940-70-2; CuCOCl, 53513-40-9.

Supplementary Material Available: A listing of observed and calculated structure factors and Table SI listing anisotropic and isotropic temperature factors (11 pages). Ordering information is given on any current masthead page.

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Molybdoarsinate Heteropoly Complexes. Structure of the Hydrogen Tetramolybdodimethylarsinate(2–) Anion by X-ray and Neutron Diffraction[1]

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Received December 11, 1979

Seven salts of the heteropoly molybdate anions $R_2AsMo_4O_{15}H^{2-}$ (R = CH_3, C_2H_5, C_6H_5) have been synthesized and characterized by spectroscopic measurements. The structure of $[(CN_3H_6)_2AsMo_4O_{15}H]\cdot H_2O$ ($P2_1/c$, a = 8.531 (2) Å, b = 8.527 (2) Å, c = 30.129 (5) Å, β = 95.49 (2)°) has been determined by single-crystal X-ray and neutron diffraction and refined to final consistency indices R and R_w of 0.043 and 0.063 for the X-ray data and 0.047 and 0.037 for the neutron data. The anion may be viewed as a ring of face- and edge-shared MoO_6 octahedra capped by the tetrahedral $(CH_3)_2AsO_2^-$ group. At the base of the anion is an oxygen that is asymmetrically shared by all four Mo atoms (Mo–O = 2.360–2.927 Å). The single anionic proton required by the stoichiometry is located on the basal oxygen, with an O–H bond length of 0.991 (5) Å. The unique hydrogen participates in a hydrogen bond to a water molecule which is 1.779 (5) Å away from the hydrogen.

Introduction

A novel class of heteropoly compounds containing organic groups covalently bound to a surface heteroatom has attracted much attention.[4-10] Some representatives of this class are $(CN_3H_6)_5[(C_6H_5As)_2W_6O_{25}H]\cdot 2H_2O$,[5] $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$,[6] $K_4[\alpha\text{-}(\eta^5\text{-}C_5H_5)Ti(PW_{11}O_{39})]$,[7] $[(C_5H_5)Fe(CO)_2Ge]_2W_{11}PO_{40}^{3-}$,[8] $(CN_3H_6)_4[(C_6H_5As)_2Mo_6O_{25}H_2]\cdot 4H_2O$,[9a,b] and $H_4[(p\text{-}H_2NC_6H_4As)_4Mo_{12}O_{46}]\cdot 10CH_3CN\cdot H_2O$.[10] These few examples illustrate the diversity in heteroatom, organic group, and overall composition which allows these compounds to exhibit a promising mixture of properties inherent to ionic metal oxides and covalent organic groups. We report here the synthesis and structural characterization of some of these organometalates which have the general formula $R_2AsMo_4O_{15}H^{2-}$. Salts of anions with this stoichiometry were first prepared by Rosenheim and Bilecki.[11]

Since the formula indicated a totally new structural type, single-crystal X-ray and subsequent neutron diffraction measurements were undertaken on $(CN_3H_6)_2[(CH_3)_2AsMo_4O_{15}H]\cdot H_2O$. Following our preliminary report[12] of the X-ray structure we learned of an independent determination by Matsumoto.[13] Klemperer et al.[14] have reported the ^{17}O NMR spectra of the dimethyl and diphenyl derivatives. Recently, an analogous structure has been reported[15] for the tetra-*n*-butylammonium salt of $[H_2CMo_4O_{15}H]^{3-}$ and has been proposed[16] for $Mo_5O_{17}H^{3-}$.

Experimental Section

Preparation of Complexes. Tetramolybdodimethylarsinate: Guanidinium Salt. Dimethylarsinic acid (1.4 g, 0.01 mol) and sodium molybdate (9.8 g, 0.04 mol) were dissolved in 50 mL of water, and the solution was boiled for 15 min. After being cooled, the solution

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