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Synthesis, Characterization, and Crystal and Molecular Structure of $(NH_4)_2[Cu(NH_3)_2(MoO_4)_2]$

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Light blue crystals of the title compound were grown from aqueous solution. The compound was characterized by chemical analysis, infrared spectroscopy, thermogravimetric analysis, magnetic susceptibility, and ultraviolet–visible spectroscopy. The crystal and molecular structure has been determined by X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$, with one molecule per unit cell and lattice parameters $a = 6.155(3)$, $b = 7.158(3)$, and $c = 7.516(2)$ Å; $\alpha = 108.52(6)$, $\beta = 93.99(6)$, and $\gamma = 113.72(4)°$. Anisotropic refinement on 987 unique reflections led to $R_w = 0.041$. The geometry at Cu in the $[Cu(NH_3)_2(MoO_4)_2]^{2-}$ anion is square planar with a *trans* arrangement of ammonia and molybdate ligands.

Introduction

An earlier investigation of the leaching of copper-bearing molybdenite concentrate with nitric acid yielded, among other products, small crystals of a compound of composition $(NH_4)_2Cu(MoO_4)_2(NH_3)_2$. Subsequent experiments revealed that, in fact, several ammonium–copper molybdates can be isolated from the reaction of aqueous solutions of ammonium heptamolybdate with copper sulfate. The compositions are dependent on both concentration and pH. Thermal decomposition of the resulting solids afforded cupric molybdates. Such species are of great interest for powder metallurgy applications that demand high purity raw materials.

The synthesis and structural characterization of several copper molybdates have been reported in the literature (*1–6*). However, the preparation of most of these phases involved hydrothermal solid-state reactions of cuprous oxide and molybdenum trioxide. A few ammonia-containing copper molybdates have also been reported (*7, 8*) but no crystal chemistry data were given.

The present paper describes the synthesis, characterization, and structure determination of the title compound. X-ray diffraction powder data for this compound have been published recently (*9*).

Experimental

Instrumental. Thermogravimetric data were obtained in a Netsch differential thermal analyzer. Infrared spectra were registered on a Perkin-Elmer model 735-B spec-

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trophotometer using KBr discs and Nujol mulls. Magnetic susceptibilities were measured on a Cahn balance by the Faraday method. Ultraviolet–visible spectra were registered on a Carl-Zeiss model DMR-22 spectrophotometer. Densities were determined by pycnometry in water.

Intensity data were collected with an Enraf-Nonius CAD-4 four circle diffractometer using graphite-monochromated MoK_α radiation and the Θ–2Θ scan technique. The lattice parameters were derived from the setting angles of 25 diffractometer centered reflections and refined by conventional least squares procedures. Intensity data for 1071 reflections (h, -7 to 7; k, -8 to 8; l, 0 to 8) were collected, of which 987 were unique and 781 observed with $F > 3\sigma$. The crystal structure was solved by Patterson methods and the positions and anisotropic thermal parameters for all non-H atoms were refined by full matrix least squares cycles to final R and R_w values of 0.046 and 0.041, respectively. The weighting scheme was based on the equation $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. All calculations were carried out with the SHELX76 program (*10*).

Synthesis. The following equations illustrate the processes involved in the leaching of molybdenite (*11, 12*). The specific step which leads to the formation of the title compound is shown in Eq. (2).

Molybdenite + Oxidant ⇒

Soluble material + Insoluble material (1)

(Soluble material, products of reduction of the oxidant, and oxidation of the sulfur of the molybdenite, Cu^{2+}, Fe^{3+}, Mo(V), or Mo(VI); insoluble material, $MoO_3 \cdot xH_2O$, SiO_2)

Insoluble material + Ammonia ⇒

Soluble materials + Insoluble (2)

(Soluble material, products from the equilibria of formation of ammonium molybdates and polymolybdates, eventual formation of cupric or ferric complexes)

Ammonium molybdates + Acid ⇒ Crystalline molybdates (3)

Crystalline molybdates + Heat ⇒ MoO_3 (Pure) (4)

Results and Discussion

General characterization of the compound. Analytical results (found: Cu, 14.5; Mo, 40.2; N, 12.40; H, 3.06%; calculated for $CuMo_2O_8N_4H_{14}$: Cu, 14.01; Mo, 42.31; N, 12.35; H, 3.11%) suggest a $(NH_4)_2Cu(NH_3)_2(MoO_4)_2$ formulation.

Figure 1 shows the thermogravimetric results. There are two zones which correspond to the loss of ammonia and ammonium. One of the zones, exothermic and located in the range 220–280°C, is tentatively assigned to the presence of ammonia; the other, endothermic and located at 343°C, is probable due to the presence of ammonium (*13*).

Table I lists the infrared spectra, in the 4000–400 cm^{-1} region, together with the respective assignment for coordinated ammonia and the ammonium cation (*14*). The presence of bands at 895(s), 840(s,br), and

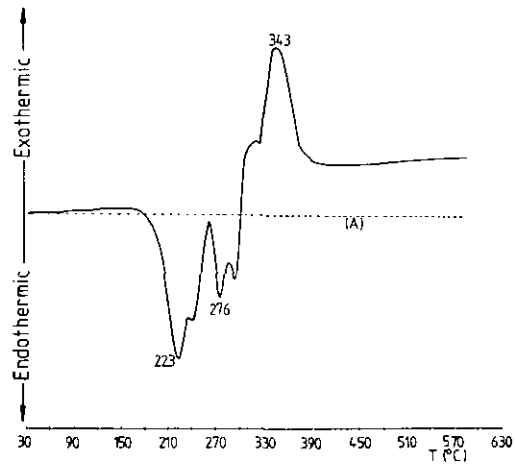

FIG. 1. Differential thermal analysis for $(NH_4)_2[Cu(NH_3)_2(MoO_4)_2]$.

TABLE I

INFRARED SPECTRA AND ASSIGNATIONS[a] FOR $(NH_4)_2(Cu(NH_3)_2(MoO_4)_2)$[b]

Band	Assignment	Band	Assignment
3300(s)	$\mu_3(Cu-NH_3)$	1590(m)	$\mu_4(Cu-NH_3)$
3180(s)	$\mu_1(Cu-NH_3)$	1450(s)	$\mu_4(NH_4^+)$
3140(s)	$\mu_3(NH_4^+)$	1410(s)	$\mu_4(NH_4^+)$
2975(s)	$\mu_1(NH_4^+)$	1225(s)	$\mu_2(Cu-NH_3)$
2925(s)	$\mu_2 + \mu_4(NH_4^+)$	895(s)	$\mu_1(MoO_4)$
2800(s)	$2\mu_4(NH_4^+)$	840(s)	$\mu_3(MoO_4)(A_1)$
2040(s)	$\mu_2 + \mu_6(NH_4^+)$	795(s)	$\mu_3(MoO_4)(E)$
1840(m)	$\mu_4 + \mu_6(NH_4^+)$	710(s)	$\mu_5(Cu-NH_3)$
1610(m)	$\mu_2(NH_4^+)$	495(w)	$\mu(Cu-O)$

[a] See Ref. (*14*).

[b] Values in cm^{-1}; (s), strong; (m), medium; (w), weak; (br), broad.

795(s) cm^{-1}, shows that the molybdate is not present in a polymeric form (*14–17*) and suggests that the molybdate is monocoordinated (*17*).

The room temperature magnetic moment of the compound, ca. 1.73 Bohr magnetons, suggests the absence of Cu(II)–Cu(II) interactions in solid phase (*18*). The ultraviolet–visible spectrum of the title compound reveals a single asymmetric band at 14,400 cm^{-1} with a shoulder at ca. 10,800 cm^{-1}. These spectral features are assigned to *d–d* transitions in an essentially planar copper(II) complex (*19*), i.e., $d_{x^2-y^2} \rightarrow d_{xy}$, d_{xz}, d_{yz}, for the main band, and $d_{x^2-y^2} \rightarrow d_{z^2}$, for the shoulder.

TABLE II

CRYSTAL DATA FOR $(NH_4)_2(Cu(NH_3)_2(MoO_4)_2)$

Space group	$P\bar{1}$
a (Å)	6.155(3)
b (Å)	7.158(3)
c (Å)	7.516(4)
α (°)	108.52(6)
β (°)	93.99(6)
γ (°)	113.72(4)
V (Å^3)	279.94(46)
FW (amu)	453.56
Z	1
D_x (mg m^{-3})	2.69
D_{293} (mg m^{-3})	2.64
μ(Mo$K\alpha$) (cm^{-1})	41.01
Transmission factors	0.433–0.819
Crystal shape	Parallelepiped bound by (100), (010), (001)
Crystal size (mm × mm × mm)	0.1 × 0.125 × 0.25

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE STRUCTURE OF $(NH_4)_2[Cu(NH_3)_2(MoO_4)_2]$

(a) MoO_4 tetrahedron			
Mo–O(1)	1.749(7)	O(1)–O(3)	2.918(9)
Mo–O(2)	1.724(6)	O(1)–O(4)	2.858(11)
Mo–O(3)	1.797(7)	O(2)–O(3)	2.862(10)
Mo–O(4)	1.751(7)	O(2)–O(4)	2.834(10)
O(1)–O(2)	2.784(7)	O(3)–O(4)	2.939(10)
O(1)–Mo–O(2)	106.7(3)	O(2)–Mo–O(3)	108.7(3)
O(1)–Mo–O(3)	110.7(3)	O(2)–Mo–O(4)	109.3(3)
O(1)–Mo–O(4)	109.5(3)	O(3)–Mo–O(4)	111.9(4)
(b) Cu coordination			
Cu–O(3)	1.997(7)	Cu–N(1)	2.012(8)
N(1)–Cu–O(3)	90.2(3)	Cu–O(3)–Mo	127.6(3)
(c) Shortest NH_4^+–NH_4^+ distance greater than 4.0 Å			
(d) Possible hydrogen bonds			
N(2)–O(1)	2.869(11)	N(2)–O(2)	2.882(11)
N(2)–O(3)	2.817(7)	N(2)–O(4)	2.794(10)

Crystal and molecular structure. Crystal data for the title compound are collected in Table II (*20*) and interatomic distances and bond angles appear in Table III. Table IV contains the atomic positional coordinates and the equivalent isotopic thermal parameters, and Table V lists the anisotropic thermal parameters.

TABLE IV

ATOMIC POSITIONAL COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $(NH_4)_2$ $[Cu(NH_3)_2(MoO_4)_2]$

Atom	x	y	z	B_{eq}[a]
Cu	0.5	0.5	0.5	2.02
Mo	0.7922(2)	0.2093(2)	0.2782(2)	1.58
O(1)	0.047(1)	0.287(1)	0.454(1)	2.44
O(2)	−0.300(1)	−0.063(1)	0.135(1)	2.66
O(3)	−0.452(1)	0.231(10)	0.387(1)	2.15
O(4)	−0.125(1)	0.370(1)	0.138(1)	2.59
N(1)[b]	−0.577(1)	−0.490(1)	0.237(1)	2.33
N(2)[c]	−0.099(2)	0.152(1)	−0.235(1)	2.62

[a] $B_{eq} = \frac{8}{3}\pi^2\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_ia_j$.

[b] N(1), ammonia nitrogen atom (as deduced from N–Cu distance).

[c] N(2), ammonium nitrogen atom.

TABLE V

ANISOTROPIC THERMAL PARAMETERS FOR ATOMS IN $(NH_4)_2[Cu(NH_3)_2(MoO_4)_2]$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.0189(9)	0.0266(10)	0.0229(11)	0.0130(8)	0.0089(8)	0.0081(9)
Mo	0.0102(4)	0.0211(5)	0.0214(6)	0.0073(4)	0.0074(4)	0.0067(4)
O(1)	0.0076(34)	0.0439(47)	0.0282(47)	0.0088(33)	0.0024(32)	0.0148(41)
O(2)	0.0191(38)	0.0313(42)	0.0415(53)	0.0184(34)	0.0145(37)	0.0099(41)
O(3)	0.0144(34)	0.0231(38)	0.0357(49)	0.0100(31)	0.0167(35)	0.0095(37)
O(4)	0.0347(45)	0.0237(40)	0.0281(48)	0.0121(36)	0.0067(39)	0.0101(38)
N(1)	0.0208(48)	0.0396(54)	0.0189(52)	0.0170(43)	0.0050(40)	0.0132(46)
N(2)	0.0306(52)	0.0318(53)	0.0245(58)	0.0109(44)	0.0140(46)	0.0126(48)

[a] Anisotropic temperature factors in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$.

The structure of the diammin dimolybdate cuprate(II) anion is illustrated in Fig. 2, and the packing diagram for this anion is shown in Fig. 3.

The geometry at copper in the $[Cu(NH_3)_2(MoO_4)_2]^{-2}$ anion is square planar with a *trans* arrangement of ammonia and molybdate ligands. The planarity is absolute because the copper atom is located in a center of inversion. The two MoO_4 tetrahedra are ligated in a monodentate fashion.

There is no evidence for Cu . . . Cu interactions. However, as shown in Fig. 3 there is a weak interaction between Cu and MoO_4 as indicated by dotted lines. The distance Cu–O(1) is 2.52 Å.

The NH_4^+ cations preferentially occupy sites near the terminal O atoms of the tetrahedra, with a minimum ammonium–ammonium distance greater than 4.0 Å which satisfies the shortest distance criterion for cation location.

Bond distances in the copper plane are: 1.997 Å for Cu–O, and 2.012 Å for Cu–N. Mo–O distances range from 1.724 to 1.797 Å in the tetrahedra; and the O–Mo–O an-

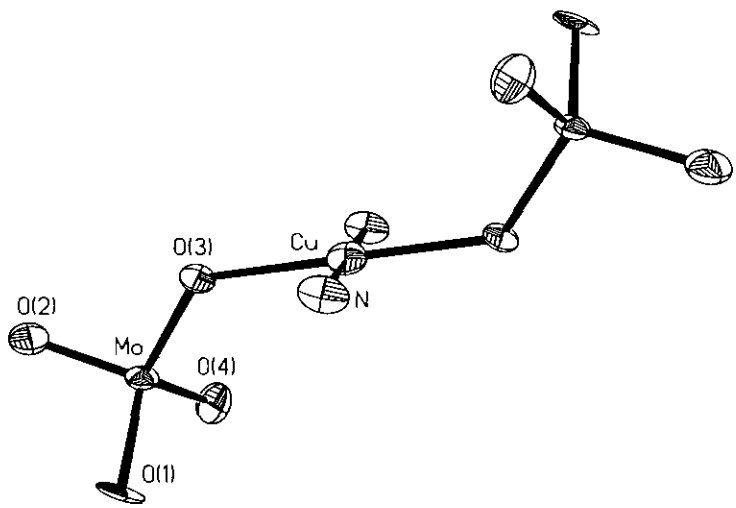

FIG. 2. Ortep plot for diammin dimolybdate cuprate(II). The thermal ellipsoids are at 50% probability.

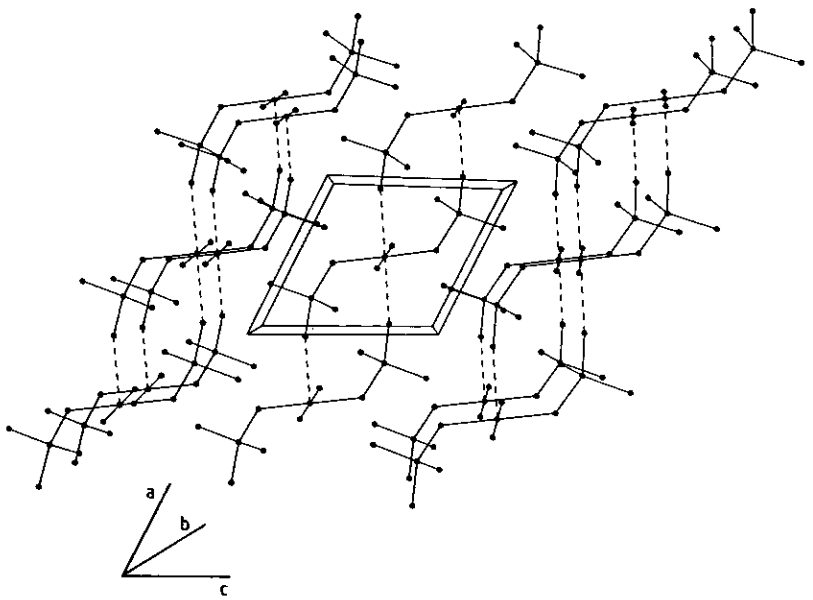

FIG. 3. Packing structure for ammonium diammin dimolybdate cuprate(II).

gles vary from 106.6 to 111.9° (see Table III and Fig. 2).

Extensive information is available on the structures and characterization of copper(II) molybdates, mainly obtained by other methods (*1, 4, 5*). To our knowledge, this is the first X-ray crystal structure for a copper(II) molybdate which contains both ammonium and ammonia.

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