Acknowledgment. We thank the Science Research Council and the University of London Central Research Fund (NMR crystal filter) for support and Johnson Matthey Ltd. for the loan of Au. We also thank Dr. M. Hursthouse (Queen Mary College) for use of his SRC-supported X-ray data collection service and Dr. J. Feeney and a reviewer for useful discussion.

Registry No. $[n\text{-}Bu_4N][Au(S_2C_7H_6)_2]$, 77880-82-1; $[Et_4N][Au(S_2C_7H_6)_2]$, 77880-83-2; $[Me_4N][Au(S_2C_7H_6)_2]$, 77880-84-3; SO_2, 7446-09-5; $NaAuCl_4$, 15189-51-2.

Supplementary Material Available: A listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Synthesis, Structure, and Properties of Cluster Compounds with D-Penicillamine Containing Cu^I, Cu^{II}, Ag^I, Ni^{II}, and Pd^{II}. X-ray Structure of Pentakis(hexaamminecobalt(III)) Tris[μ_8-chloro-*octahedro*-hexakis[μ_4-[*cis*-bis(D-pencillaminato(2−)-*N*,*S*)nickel(II)]-*S*,*S*′]-*cubo*-octaargentate(I)]-*n*-Water, $[Co(NH_3)_6]_5[Ag^I{}_8Ni^{II}{}_6(SC(CH_3)_2CH(NH_2)COO)_{12}Cl]_3\cdot{\sim}197H_2O$

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Metal thiolate cluster compounds of composition $[M^I{}_8M^{II}{}_6L_{12}Cl]^{5-}$ have been prepared with M^I = Cu^I or Ag^I, M^{II} = Cu^{II}, Ni^{II}, or Pd^{II}, and L = the deprotonated penicillamine ligand $(SC(CH_3)_2CH(NH_2)COO)^{2-}$. The X-ray crystal structure of $[Co(NH_3)_6]_5[Ag_8Ni_6L_{12}Cl]_3\cdot{\sim}197H_2O$ has been solved. The compound crystallizes in the cubic space group *F*432 with a = 51.774 (7) Å and with 32 cluster anions per unit cell. The intensities of 2927 reflections with $I > 2\sigma(I)$ were measured on an automatic diffractometer using Mo Kα radiation. The structure was solved by heavy-atom methods and refined with unit weights by using block-diagonal least-squares methods and a Waser constraints procedure. The final residual R is 0.058. Each $[Ag_8Ni_6L_{12}Cl]^{5-}$ ion lies on a threefold axis. It contains several regular atomic polyhedra. A Cl^--centered Ag_8 cube is inscribed into an icosahedron of S atoms. Each S atom functions as a bridging ligand between two Ag^I atoms and a Ni^{II} atom. The Ag atoms are planar coordinated by three S atoms with the common central Cl^- as a weak fourth ligand at ~3.0 Å. The six Ni^{II} atoms lie at the apices of an octahedron (edge ~ 7.0 Å). Each Ni^{II} atom is square-planar cis-bidentate coordinated by two S and two N atoms. The crystal structure is stabilized by hydrogen bonds between adjacent cluster anions, water molecules, and $Co(NH_3)_6{}^{3+}$ ions. Only the Cu^{II}-containing compounds of this composition are paramagnetic. The ESR and NMR parameters of the complexes are presented. The ESR spectra of Cu^{II}-doped diamagnetic clusters show that the unpaired electron is localized on the Cu^{II} atom.

Introduction

The complex formation of thiolate ligands with Cu^{II} is often complicated by simultaneous redox reactions. With thiolate ligands capable of forming five-membered chelate rings, intensely colored mixed-valence Cu^I–Cu^{II} complexes can be formed.[1] Such compounds are rather unstable unless there are two alkyl substitutents on the carbon atom adjacent to sulfur. Examples of such ligands are penicillamine (H_2Pen, $HSC(CH_3)_2CH(NH_2)COOH$), α-mercaptoisobutyric acid (H_2MIBA, $HSC(CH_3)_2COOH$), and β,β-dimethylcysteamine (HDMC, $HSC(CH_3)_2CH_2NH_2$).[2] X-ray structure determinations have shown that complex ions of composition $[Cu^I{}_8Cu^{II}{}_6L_{12}Cl]^z$ are formed, where L is the deprotonated thiolate ligand Pen (z = 5−),[3] MIBA (z = 5−),[4] or DMC (z = 7+).[5] The structure of these compounds is schematically depicted in Figure 1. Each of the Cu(I) atoms in the structure is bound by three sulfur atoms in a trigonal coordination geometry. The central chloride ion in the structure is a weak ligand bridging between the eight Cu^I atoms (Cu^I–Cl ≈ 2.8 Å). The Cu^{II} atoms are four-coordinated by two sulfur and two nitrogen atoms in a cis-bidentate coordination geometry.

We now show that the formation of such cluster compounds is not restricted to copper. Other metals accepting similar coordination geometries stabilize similar cluster structures. With D-penicillamine as a ligand, clusters were obtained not only with Cu^I and Cu^{II} but also with Ag^I, Ni^{II}, and Pd^{II}. Compounds containing the metal combinations shown in Table I have been prepared. Only the Cu^{II}-containing complexes are paramagnetic. A ferromagnetic exchange interaction couples the unpaired spins on the six Cu^{II} sites in the structure, resulting in an S = 3 ground state.[5,6] All other compounds

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[1] Klotz, I. M.; Czerlinski, G. H.; Fiess, H. A. *J. Am. Chem. Soc.* **1958**, *80*, 2920.

[2] Abbreviations used in this article: H_2Pen = D-penicillamine, $HSC(CH_3)_2CH(COO^-)NH_3{}^+$; H_2MIBA = α-mercaptoisobutyric acid, $HSC(CH_3)_2COOH$; HDMC = β,β-dimethylcysteamine, $HSC(CH_3)_2CH_2NH_2$; PenSSPen = penicillamine sulfide. The deprotonated ligands are abbreviated as Pen, MIBA, and DMC, respectively. M = metal, L = ligand.

[3] (a) Birker, P. J. M. W. L.; Freeman, H. C. *J. Chem. Soc., Chem. Commun.* **1976**, 312; (b) *J. Am. Chem. Soc.* **1977**, *99*, 6890.

[4] Birker, P. J. M. W. L. *Inorg. Chem.* **1979**, *18*, 3502.

[5] (a) Schugar, H. J.; Ou, C. C.; Thich, J. A.; Lalancette, R.; Furey, W.; Jr. *J. Am. Chem. Soc.* **1976**, *98*,, 3047. (b) Schugar, H. J.; Ou, C. C.; Thich, J. A.; Potenza, J. A.; Felthouse, T. R.; Haddad, M. S.; Hendrickson, D. N.; Furey, W.; Jr.; Lalancette, R. A. *Inorg. Chem.* **1980**, *19*, 543.

[6] van Kempen, H.; Perenboom, J. A. A. J.; Birker, P. J. M. W. L. *Inorg. Chem.* **1981**, *20*, 917.

Table I. Spectral and Magnetic Data for the Mixed-Valence Penicillamine Compounds of Composition $[M^I{}_8M^{II}{}_6Pen_{12}Cl]^{5-}$

		visible spectrum[a]		NMR spectrum[b]				
$M^I{}_xM^{II}{}_y$	color	ν_{max}, cm^{-1}	ϵ, mol^{-1} dm^3 cm^{-1}	α-CH	CH_3	CH_3	IR spectrum $\nu(COO)$, cm^{-1}	magnetic properties
$Cu^I{}_8Cu^{II}{}_6$	purple	19 300	25 500				1597[f]	ref 6
$Cu^I{}_8Ni^{II}{}_6$	brown	. . .[c]					1598[f]	*h*
$Ag^I{}_8Ni^{II}{}_6$	red	21 700[d]	1 050[e]	3.96	2.58	1.79	1600[g]	diamag
$Ag^I{}_8Pd^{II}{}_6$	yellow	. . .[c]		3.37	2.25	2.63	1612[g]	diamag
$Cu^I{}_8Ni_{10}$	brown	insol					1612[f]	$X_M = 19\,776 \times 10^{-6}$ [i]

[a] Measured in 0.2 M sodium acetate buffer. [b] Measured in D_2O at 99.5 MHz. δ values vs. reference $[(CH_3)_3SiCD_2CD_2COONa]$. [c] No absorption maximum below 27 000 cm^{-1}. [d] This band can be assigned to the $^1A_{g1g} \rightarrow {}^1B_{1g}$ transition for square-planar Ni^{II}. [e] This band lies on the slope of a strong absorption in the UV region. The value of ε may therefore be exaggerated. [f] Measured on the Na^+ salt. [g] Measured on the $Co(NH_3)_6{}^{3+}$ salt. [h] Varying degrees of weak paramagnetism measured (see text). [i] X_M in cm^3 mol^{-1} corrected for diamagnetism at 25 °C; the effective Bohr Magneton number μ_{eff} is 3.4 per octahedral Ni^{II} atom (see text).

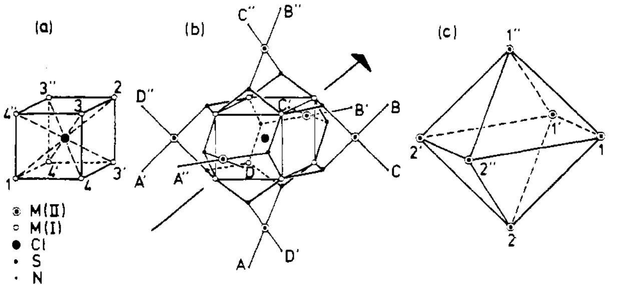

Figure 1. Schematic structure of mixed-valence penicillamine clusters of composition $[M^I{}_8M^{II}{}_6Pen_{12}Cl]^{5-}$: (a) the central Cl-centered $M^I{}_8$ cube, showing the numbering of Ag^I atoms used in the text; (b) the $ClM^I{}_8S_{12}M^{II}{}_6N_{12}$ core of the complex ion on the same scale (ligand carbon and oxygen atoms have been omitted for clarity; the letter codes near the nitrogen atoms of the penicillamine ligands are the labels of the crystallographically independent ligands as used in the text); (c) the octahedron of M^{II} atoms, showing the numbering of Ni^{II} atoms used in the text.

containing planar-coordinated d^8 and d^{10} transition-metal ions are diamagnetic.

The X-ray structure of the $Co(NH_3)_6{}^{3+}$ salt of one of these new diamagnetic cluster anions, $[Ag^I{}_8Ni^{II}{}_6Pen_{12}Cl]^{5-}$, is presented. It proves the structural similarity with the parent $Cu^I{}_8Cu^{II}{}_6$ cluster and has been refined to a greater accuracy than the latter. A preliminary communication about the synthesis and spectroscopy of these compounds has been published.[7]

Experimental Section

Materials. D-Penicillamine (Aldrich, Gold Label) was used without further purification. All other reagents and solvents were of commercially available reagent grade quality.

Preparations. General Information. All preparations were carried out in 0.2 M sodium acetate buffer at ambient temperatures unless stated otherwise. The compounds are formed by the combination of stoichiometric amounts of the constituent metals and the ligand according to eq 1. For the preparation of the Cu^I-containing compounds an extra amount of D-penicillamine is added to reduce Cu^{2+} in situ to Cu^I (eq 2). If only a small volume of the buffer is used for this reaction, an insoluble complex is formed, which is analyzed as $Na_5Cu_8Ni_{10}Pen_{16}Cl\cdot 31H_2O$ (see Discussion).

$$6M^{2+} + 8M^{+} + 12Pen + Cl^{-} \rightarrow [M^I{}_8M^{II}{}_6Pen_{12}Cl]^{5-} \quad (1)$$

$$6Ni^{2+} + 8Cu^{2+} + 20Pen + Cl^{-} \rightarrow [Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl]^{5-} + 4PenSSPen \quad (2)$$

$[Co(NH_3)_6]_5[Ag^I{}_8Ni^{II}{}_6Pen_{12}Cl]_3\cdot{\sim}197H_2O$. To 20 mL of the buffer solution containing 150 mg (1 mmol) of D-penicillamine was added a solution of 119 mg (0.5 mmol) of $NiCl_2\cdot 6H_2O$ in 1 mL of water. The solution turned from brown to red upon addition of a solution of 113 mg of $AgNO_3$ in 1 mL of water. In a test tube (diameter 3 cm) a layer of 5 mL of water was introduced over this red solution by using a Pasteur pipet. A warm solution of 35 mg of $Co(NH_3)_6Cl_3$ in 5 mL of water was gently added to this upper layer. After 24 h red crystals of the complex had grown on the wall of the test tube. The crystals that were used for chemical analyses were isolated after 5 days, washed with alcohol, and dried in air. Anal. Calcd for $Co_5Ag_{24}Ni_{18}C_{180}H_{808}N_{66}S_{36}O_{269}Cl_3$: Co, 2.19; Ag, 19.31; Ni, 7.88; C, 16.13; H, 6.07; N, 6.90; S, 8.61; Cl, 0.79. Found: Co, 2.14; Ag, 18.5; Ni, 8.21; C, 16.91; H, 5.83; N, 6.80; S, 8.57; Cl, 0.7.

$[Co(NH_3)_6]_5[Ag^I{}_8Pd^{II}{}_6Pen_{12}Cl]_3\cdot{\sim}111H_2O$. A mixture of 150 mg (1 mmol) of D-penicillamine and 88 mg (0.5 mmol) of $PdCl_2$ was stirred in 25 mL of the buffer solution at 50 °C. After 1 h the orange solution was cooled to room temperature and a solution of 113 mg (0.66 mmol) of $AgNO_3$ in 1 mL of water was added. The yellow solution thus obtained was filtered. The yellow sodium salt of the complex was precipitated with 35 mL of alcohol, filtered off, and washed with alcohol and ether. It was subsequently dissolved in 5 mL of the buffer solution. The solution was centrifuged at 4000 rpm for 10 min. The clear yellow supernatant was decanted into a test tube, and a warm solution of 12 mg of $Co(NH_3)_6Cl_3$ in 2 mL of water was layered on top. After a few hours the first crystals had grown on the wall of the test tube. After 4 days the yellow needles were isolated and washed with alcohol. Anal. Calcd for $Co_5Ag_{24}Pd_{18}C_{180}H_{636}N_{66}S_{36}O_{183}Cl_3$: Co, 2.32; Ag, 20.34; Pd, 15.07; C, 17.01; H, 5.04; N, 7.27; S, 9.07. Found: Co, 2.28; Ag, 20.4; Pd, 15.4; C, 17.09; H, 5.03; N, 7.38; S, 8.86.

$Na_5[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl][Ni^{II}Pen]_4\cdot{\sim}31H_2O$. In 10 mL of the buffer solution was dissolved 250 mg (1.66 mmol) of D-penicillamine. A solution of 119 mg (0.5 mmol) of $NiCl_2\cdot 6H_2O$ in 2 mL of water was added. The color of the resulting brown solution became much more intense when 113 mg (0.66 mmol) of $CuCl_2\cdot 2H_2O$ was added dropwise under vigorous stirring. After 30 min a brown precipitate of the complex had formed. It was filtered off and washed with water, ethanol, and ether; yield 200 mg. Anal. Calcd for $Na_5Cu_8Ni_{10}C_{80}H_{206}N_{16}S_{16}O_{63}Cl$: Cu, 12.22; Ni, 14.11; C, 23.10; H, 4.99; N, 5.38; S, 12.33. Found: Cu, 12.5; Ni, 14.6; C, 23.11; H, 5.29; N, 5.30; S, 11.88.

$Na_5[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl]\cdot{\sim}40H_2O$. To 50 mL of the buffer solution containing 250 mg of D-penicillamine was added a solution of 119 mg (0.5 mmol) of $NiCl_2\cdot 6H_2O$ in 2 mL of water. This solution was stirred, and 113 mg (0.66 mmol) of $CuCl_2\cdot 2H_2O$ in 4 mL of water was added dropwise. The brown solution thus obtained was kept for 12 h. The insoluble material was filtered off, and 100 mL of ethanol was added to the filtrate. After 2 h the precipitate was carefully filtered off and washed with alcohol and ether. Care must be taken that no air is sucked through the precipitate before it has been washed thoroughly with alcohol and ether; yield 160 mg. Anal. Calcd for $Na_5Cu_8Ni_6C_{60}H_{188}N_{12}S_{12}O_{64}Cl$: Cu, 14.53; Ni, 10.07; C, 20.60; H, 5.42; N, 4.81; S, 11.00. Found: Cu, 14.8; Ni, 9.62; C, 21.81; H, 5.57; N, 4.84; S, 9.77.

Physical Measurements. Magnetic susceptibility measurements were carried out with use of the Faraday method. Infrared spectra were measured on a Perkin-Elmer 580 spectrometer. UV-visible spectra were measured on a Beckman DK-2A spectrophotometer. X-Band ESR spectra were measured at 120 K in frozen aqueous solution on a Varian E3 ESR spectrometer. NMR spectra at 100 MHz were recorded on a JEOL-PS 100 NMR spectrometer. Elemental analyses were carried out by Pascher Mikroanalytisches Laboratorium, Bonn, West Germany.

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(7) Birker, P. J. M. W. L. *J. Chem. Soc., Chem. Commun.* **1980**, 946.

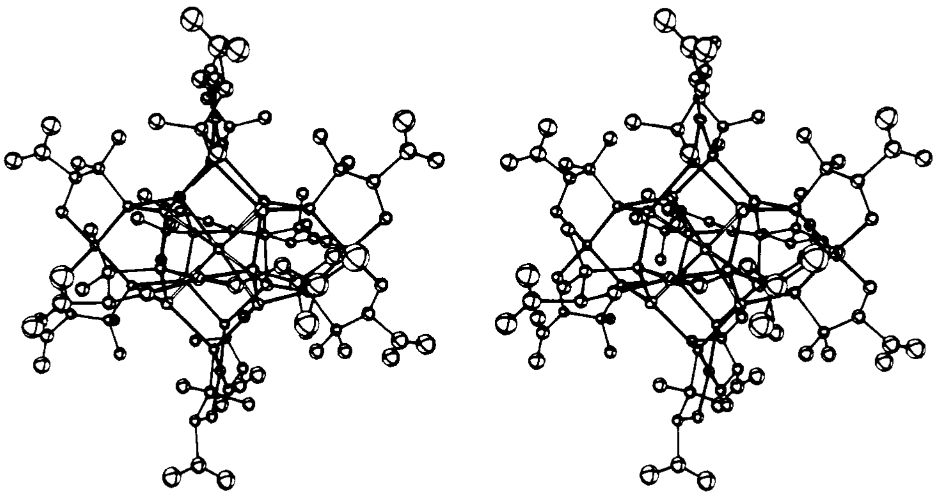

Figure 2. Stereo drawing of $[Ag^I_8Ni^{II}_6Pen_{12}Cl]^{5-}$. The thermal vibration ellipsoids of the atoms are shown (probability 20%).

X-ray Diffraction Measurements and Data Reduction. The crystals were sealed in capillary tubes to reduce deterioration. Preliminary precession photographs showed that $[Co(NH_3)_6]_5[Ag^I_8Ni^{II}_6Pen_{12}Cl]_3 \cdot \sim 197H_2O$ crystallizes in the cubic space group $F432$. This space group is uniquely determined by the systematic absences for odd values of $h + k$, $k + l$, and $h + l$, by the Laue symmetry $m3m$ and by the presence of a chiral ligand. All further diffraction measurements were carried out with use of graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å) on a Nonius CAD4 automatic diffractometer using a crystal of 0.3 × 0.3 × 0.5 mm. Accurate cell dimensions (a = 51.774 (7) Å) were determined from the positions of 25 automatically centered strong reflections ($\theta > 7°$). The density measured by flotation of superficially dried crystals in a $CHCl_3$–$C_2H_4Br_2$ mixture is 1.71 (1) g cm^{-3}. This value agrees well with the calculated value of 1.711 g cm^{-3} based on the elemental analysis (see above) for 32 cluster anions per unit cell. A complete set of data was measured ($\theta < 22°$) consisting of 4112 independent reflections. Profile analysis of a suitable reflection led to the selection of the ω-$(^2/_3)2\theta$ scan mode. The extremely narrow mosaic spread allowed an ω-scan angle of $(0.40 + \tan \theta)°$. The crystal-to-counter distance was 173 mm. The vertical detector aperture was 4 mm and the horizontal aperture was $(1.10 + 2 \tan \theta)$ mm. The scan speeds were determined by a required precision of $I > 50\sigma(I)$ with a maximum scan time of 120 s/reflection. Background correction and calculation of I and $\sigma(I)$ were carried out as described earlier.[3] Three intensity-control reflections were measured after every 5400 s of X-ray exposure time. The data were corrected for the observed decrease in intensity due to decomposition (17%). The orientation of the crystal was checked after every 200 reflections. Lorentz and polarization corrections were applied in the usual way. Absorption corrections (μ(Mo Kα) = 18.5 cm^{-1}) were applied by using the method of de Graaff.[8] Scattering factors for neutral atoms were taken from ref 9 and were corrected for anomalous scattering.

Solution and Refinement of the Structure. The title compound crystallizes in the same space group ($F432$) as the Tl^+ salt of the structurally related $[Cu^I_8Cu^{II}_6Pen_{12}Cl]^{5-}$ ion with comparable unit cell dimensions[3] (51.774 (7) and 50.847 (5) Å, respectively). The structure of the $Cu^I_8Cu^{II}_6$-containing compound was shown to consist of ordered complex anions linked by hydrogen bonds and surrounded by disordered H_2O molecules and Tl^+ ions. It was assumed that the unit cell of the $Ag^I_8Ni^{II}_6$ compound also contains 32 hydrogen-bonded complex anions surrounded by disordered $Co(NH_3)_6^{3+}$ ions and H_2O molecules. The fact that there are $(5 \times 32)/3$ $Co(NH_3)_6^{3+}$ ions per unit cell indicates that there must be some disorder. This assumption was proved by the solution of the structure. The first trial structure consisted of the Ag^I, Ni^{II}, S, and Cl atoms with the fractional positional coordinates of the Cu^I, Cu^{II}, S, and Cl atoms, respectively, in the $Cu^I_8Cu^{II}_6$-containing structure. The other atoms listed in Table II were found in a subsequent series of Fourier and difference Fourier maps. Difference Fourier syntheses revealed the positions of 14 disordered water molecules and 2 $Co(NH_3)_6^{3+}$ ions. One of the $Co(NH_3)_6^{3+}$ ions lies on a threefold axis. It was refined as a fully occupied $Co(NH_3)_6^{3+}$ ion (without hydrogen atoms) accounting for 0.60 of the total amount of $Co(NH_3)_6^{3+}$ in the structure. The second, highly distorted, $Co(NH_3)_6^{3+}$ ion lies on a fourfold axis. The Co atom herein was given a temperature factor comparable to that of the first Co atom, and its occupancy was refined. The N atoms of this $Co(NH_3)_6^{3+}$ were given the same occupancy as the Co atom, and their temperature factors were refined. The number of $Co(NH_3)_6^{3+}$ ions thus included in the refinement corresponds with 40.4 ions per unit cell, which is 0.76 of the total amount of $Co(NH_3)_6^{3+}$ (see above). There are hydrogen bonds between the $Co(NH_3)_6^{3+}$ ions and the carboxylate groups of the complex ions. The disordered water molecules were given fixed-temperature factors, and the occupancies of their positions were refined. The number of water molecules in the refinement corresponds with 491 molecules per unit cell, which is 0.23 of the total amount of water (~2100 per unit cell). The Ag, Ni, and Cl atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the ligands were included on their calculated positions and were given the isotropic thermal parameters of the atoms to which they are bonded. The structure was refined by block-diagonal least-squares methods. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1$. Attempts to refine the structure with other weighting schemes did not improve the quality of the refinement. This was also observed in the refinement of related structures.[3,4] The bond lengths in the penicillamine ligands were kept within acceptable limits with a Waser constraints procedure.[10] At the stage where the residual R value[11] was 0.062, the complete structure was inverted. A new structure factor calculation reduced this R value to 0.060, indicating that the absolute configuration was thus obtained. A total of 170 positional parameters, 72 temperature factors, and 15 occupancies were refined by using the 2927 reflections for which $I > 2\sigma(I)$. The final residual R was 0.058. A final difference Fourier synthesis showed no excursions above background. Atomic positional, vibrational, and occupancy parameters are given in Table II. A list of calculated and observed structure factors is available as supplementary material, together with a list a calculated positions for the ligand hydrogen atoms.

Description of the Structure and Comparison with Related Structures

The structure of $[Ag^I_8Ni^{II}_6Pen_{12}Cl]^{5-}$ contains several regular polyhedra of atoms, but the only crystallographic symmetry element in it is a threefold axis. A single chloride ion occupies the center of a cube of eight Ag^I atoms (see Figure 1a). Each silver atom is planar three-coordinated by penicillamine sulfur atoms. These sulfur atoms form bridges between two Ag^I atoms and one Ni^{II} atom. Each Ni^{II} atom lies above a face of the Ag^I_8 cube and is planar four-coordinated by two sulfur and two nitrogen atoms of cis-bidentate chelating penicillamine ligands (Figure 1b). The six Ni^{II} atoms in the

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(8) de Graaff, R. A. G. *Acta Crystallogr., Sect. A* **1973**, *A29*, 298.

(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–102.

(10) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091.

(11) $R = \sum||F_o| - s|F_c|| / \sum|F_o|$.

Table II. Fractional Positional Parameters,[a] Vibrational Parameters (Å^2),[b] and Occupancies[c] of Nonhydrogen Atoms[d] in $[Co(NH_3)_6]_5[Ag^I{}_8Ni^{II}{}_6Pen_{12}Cl]_3 \cdot \sim 197H_2O$

Atom	10^5x	10^5y	10^5z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{23}	10^3U_{31}
Ag(1)[e]	10606(3)	39394(3)	10606(3)	49(1)	49(1)	49(1)	-3(1)	-3(1)	3(1)
Ag(2)[e]	17198(3)	32802(3)	17198(3)	53(1)	53(1)	53(1)	3(1)	3(1)	-3(1)
Ag(3)	12215(4)	36641(4)	19734(4)	57(1)	55(1)	78(1)	4(1)	12(1)	-7(1)
Ag(4)	8583(3)	34493(3)	14521(3)	56(1)	52(1)	47(1)	4(1)	10(1)	-4(1)
Ni(1)	10684(6)	29027(5)	19625(5)	54(2)	41(2)	43(1)	-3(1)	15(1)	-6(1)
Ni(2)	8319(5)	32786(5)	6773(5)	35(2)	48(2)	36(2)	2(1)	-3(1)	-3(1)
Cl[e]	13966(9)	36034(9)	13966(9)	44(2)	44(2)	44(2)	1(2)	1(2)	-1(2)

$Co(NH_3)_6^{3+}$ ions:

Atom	10^3x	10^3y	10^3z	occupancy	10^2U_{iso}	Atom	10^3x	10^3y	10^3z	10^2U_{iso}
Co(1)[f]	0	500	69.6(7)	.087(6)	16(2)	Co(2)[e]	148.5(1)	351.5(1)	351.5(1)	16.7(4)
N(1)[f]	0	500	110(2)	.087	7(3)	N(4)	154(1)	393(1)	356(1)	26(2)
N(2)[f]	0	500	38(3)	.087	9(4)	N(5)	151.5(6)	356.8(6)	311.7(6)	14(1)
N(3)	37(2)	472(2)	75(1)	.348	12(3)					

Ligands:

Atom	10^4x	10^4y	10^4z	10^3U_{iso}	Atom	10^4x	10^4y	10^4z	10^3U_{iso}
S(A)	775(1)	3556(1)	984(1)	36(1)	S(B)	1353(1)	3202(1)	2023(1)	47(1)
C(1A)	382(3)	3609(3)	647(3)	40(5)	C(1B)	1225(4)	3035(4)	2486(4)	59(7)
C(2A)	80(4)	3612(4)	575(5)	71(8)	C(2B)	1276(6)	2935(5)	2770(5)	83(9)
C(3A)	436(3)	3648(4)	935(3)	43(6)	C(3B)	1470(4)	3121(4)	2351(3)	53(6)
C(4A)	259(4)	3481(4)	1102(4)	47(6)	C(4B)	1589(5)	3362(4)	2470(5)	71(7)
C(5A)	394(4)	3930(4)	1019(4)	56(6)	C(5B)	1677(5)	2908(5)	2322(5)	77(8)
N(A)	495(3)	3370(3)	553(3)	49(5)	N(B)	1085(3)	2833(3)	2328(3)	52(5)
O(1A)	3(5)	3835(4)	557(4)	104(6)	O(1B)	1322(5)	3109(5)	2930(4)	135(9)
O(2A)	13(5)	3395(4)	563(4)	106(6)	O(2B)	1240(5)	2702(3)	2811(3)	80(6)
S(C)	996(1)	2998(1)	1561(1)	47(1)	S(D)	783(1)	3774(1)	1807(1)	45(1)
C(1C)	821(5)	2517(4)	1645(4)	66(7)	C(1D)	456(4)	3929(4)	2174(4)	62(7)
C(2C)	615(6)	2286(6)	1646(6)	105(11)	C(2D)	188(5)	3909(6)	2333(6)	99(10)
C(3C)	742(3)	2758(3)	1483(4)	47(6)	C(3D)	518(3)	3678(4)	2028(3)	51(6)
C(4C)	755(6)	2713(6)	1193(5)	86(9)	C(4D)	621(5)	3481(5)	2218(5)	76(8)
C(5C)	478(4)	2863(5)	1556(5)	68(7)	C(5D)	290(4)	3575(5)	1868(5)	63(7)
N(C)	865(4)	2604(4)	1913(4)	62(6)	N(D)	418(3)	4143(3)	1981(3)	56(5)
O(1C)	618(5)	2173(5)	1436(5)	123(8)	O(1D)	228(5)	3794(5)	2549(5)	141(9)
O(2C)	456(5)	2273(5)	1821(5)	118(8)	O(2D)	14(5)	3994(4)	2236(4)	108(6)

Water molecules:

Atom	10^4x	10^4y	10^4z	occupancy	10^2U_{iso}	Atom	10^4x	10^4y	10^4z	occupancy	10^2U_{iso}
O(1)[e]	1968(5)	3032(5)	3032(5)	.23(2)	10.16	O(8)	475(5)	2268(5)	2623(5)	.70(3)	10.16
O(2)[e]	2290(5)	2710(5)	2710(5)	.23(2)	10.16	O(9)	1186(7)	3992(7)	3000(7)	.51(3)	10.16
O(3)[f]	0	5000	1830(9)	.19(1)	10.16	O(10)	-2036(9)	4092(9)	3456(9)	.40(3)	10.16
O(4)	66(7)	3296(7)	2706(7)	.54(3)	10.16	O(11)	664(13)	3881(13)	2860(13)	.31(3)	10.16
O(5)	216(9)	2148(9)	1035(9)	.42(3)	10.16	O(12)	571(13)	4392(13)	2759(13)	.33(3)	10.16
O(6)	-317(5)	4420(5)	2234(5)	.76(3)	10.16	O(13)	303(13)	1748(14)	1653(14)	.29(3)	10.16
O(7)	547(7)	1969(7)	2227(7)	.55(3)	10.16	O(14)[g]	0	2139(8)	2861(8)	.23(2)	10.16

[a] For explanation of labels see text. Estimated standard deviations in parentheses. [b] Temperature factors are of the form $\exp[-8\pi^2U_{iso}(\sin\theta/\lambda)^2]$ and $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. [c] Parameters without standard deviations are not separately refined (see text). The occupanices are as used in the refinement and reflect therefore the consequences of special positions and of incomplete population of atom sites. Atoms on general positions have unit occupancies. [d] A list of fractional positional parameters of hydrogen atoms is available as supplementary material. [e] Atom on threefold axis. [f] Atom on fourfold axis. [g] Atom on twofold axis.

Table III. Metal-Ligand Distances (Å), Angles (Deg), and Metal-Metal Distances (Å) in $[Co(NH_3)_6]_5[Ag_8Ni_6Pen_{12}Cl]_3 \cdot \sim 197H_2$[a]

Distances

Ag(1)–Cl	3.013 (9)	Ag(3)–S(B)	2.499 (6)	Ni(1)–S(B)	2.164 (6)	Ag(1)–Ag(4)	3.412 (2)
Ag(2)–Cl	2.897 (9)	Ag(2)–S(C'')	2.492 (6)	Ni(1)–N(B)	1.93 (2)	Ag(3)–Ag(4)	3.472 (3)
Ag(3)–Cl	3.136 (4)	Ag(3)–S(D)	2.496 (6)	Ni(1)–S(C)	2.169 (6)	Ag(3)–Ag(4'')	3.511 (3)
Ag(4)–Cl	2.913 (3)	Ag(4)–S(A)	2.524 (5)	Ni(1)–N(C)	1.89 (2)	Ag(2)–Ag(3)	3.511 (3)
Ag(1)–S(A)	2.506 (5)	Ag(4)–S(C)	2.508 (6)	Ni(2)–S(A)	2.159 (6)	Ni(1)–Ni(')	7.091 (4)
Ag(2)–S(B)	2.495 (6)	Ag(4)–S(D)	2.519 (6)	Ni(2)–N(A)	1.92 (2)	Ni(1)–Ni(2)	7.040 (4)
				Ni(2)–S(D')	2.160 (6)	Ni(1)–Ni(2'')	6.970 (4)
				Ni(2)–N(D')	1.90 (2)	Ni(2)–Ni(2')	7.147 (4)

Angles

S(A)–Ag(1)–S(A')	119.94 (1)	S(C'')–Ag(3)–S(B)	118.5 (2)	S(B)–Ni(1)–S(C)	95.4 (2)	S(A)–Ni(2)–S(D')	94.6 (2)
S(B)–Ag(2)–S(B')	119.97 (1)	S(A)–Ag(4)–S(C)	117.9 (2)	S(B)–Ni(1)–N(B)	87.7 (5)	S(A)–Ni(2)–N(A)	87.6 (5)
S(B)–Ag(3)–S(D)	120.1 (2)	S(C)–Ag(4)–S(D)	120.1 (2)	S(C)–Ni(1)–N(C)	87.7 (6)	S(D')–Ni(2)–N(D')	88.2 (6)
S(D)–Ag(3)–S(C'')	120.2 (2)	S(D)–Ag(4)–S(A)	121.9 (2)	N(B)–Ni(1)–N(C)	90.3 (8)	N(A)–Ni(2)–N(D')	90.0 (7)

[a] The primes in this table indicate the following symmetry operations: prime = $\frac{1}{2} - y$, $\frac{1}{2} - z$, x; double prime = z, $\frac{1}{2} - x$, $\frac{1}{2} - y$. The labeling of atoms and lieands is explained in Figure 1; estimated standard deviations are in parentheses.

Table IV. Comparison of Metal-Ligand and Metal-Metal Distances in $[M^I{}_8M^{II}{}_6L_{12}Cl]$ Compounds (Å)

	L = Pen			
	$Ag^I{}_8Ni^{II}{}_6$[a]	$Cu^I{}_8Cu^{II}{}_6$[b]	L = MIBA[c] $Cu^I{}_8Cu^{II}{}_6$	L = DMC[d] $Cu^I{}_8Cu^{II}{}_6$
M^I–Cl range	2.897 (9)–3.136 (4)	2.75 (5)–2.92 (3)	2.89 (7)–2.92 (7)	2.852 (3)–2.880 (3)
av	3.007	2.84	2.91	2.866
M^I–S range	2.492 (6)–2.524 (6)	2.21 (2)–2.34 (2)	2.26 (2)–2.30 (2)	2.268 (5)–2.297 (5)
av	2.503	2.27	2.28	2.282
M^{II}–S range	2.159 (6)–2.169 (6)	2.26 (3)–2.31 (3)	2.23 (2)–2.26 (2)	2.269 (6)–2.292 (6)
av	2.163	2.28	2.25	2.280
M^{II}–N/O range	1.89 (2)–1.93 (2)	2.01 (7)–2.15 (7)	1.87 (4)–1.99 (5)	1.99 (3)–2.05 (4)
av	1.91	2.08	1.93	2.02
M^I–M^I range	3.412 (2)–3.511 (2)		3.31 (1)–3.38 (1)	3.264 (4)–3.341 (3)
av	3.477	3.30	3.35	3.3
M^{II}–M^{II} range	6.970 (4)–7.147 (4)		6.29 (1)–6.87 (1)	6.645 (4)–6.825
av	7.062		6.6	

[a] This work. [b] From ref 3. [c] From ref 4. [d] From ref 5.

structure occupy the apices of an octahedron (Figure 1c). The 12 carboxylate groups are at the surface of the complex ion and are not involved in metal coordination. A stereo drawing of the complete complex ion is shown in Figure 2. The interatomic distances in the $Ag^I{}_8Ni^{II}{}_6S_{12}N_{12}Cl$ core of the complex ion are given in Table III. The interatomic distances in the ligands are constrained and are not separately listed.

The 32 cluster anions in the unit cell are packed as in the unit cell of $Tl_5[Cu^I{}_8Cu^{II}{}_6Pen_{12}Cl] \cdot nH_2O$.[3]

The structure is stabilized by hydrogen bonds between (i) $-NH_2$ and $-COO^-$ groups of adjacent complex anions, (ii) $Co(NH_3)_6{}^{3+}$ ions and $-COO^-$ groups of the complex anions, and (iii) water molecules, $Co(NH_3)_6{}^{3+}$ ions, and complex anions. The complex hydrogen-bond structure involving many disordered atoms will not be descried in further detail.

The structure of the complex is similar to that of an analogous $[Cu^I{}_8Cu^{II}{}_6Pen_{12}Cl]^{5-}$ ion and to other mixed-valence copper thiolate cluster compounds mentioned in the Introduction. The metal–ligand bond lengths in the $[M^I{}_8M^{II}{}_6L_{12}Cl]$ complexes are compared in Table IV. The structural differences between the $Ag^I{}_8Ni^{II}{}_6$ and the $Cu^I{}_8Cu^{III}{}_6$ compounds obviously result from the larger radius of the Ag^I atom and the smaller size of the Ni^{II} atom. The Ag–Cl and Ag–S bonds are longer than the corresponding Cu^I–Cl and Cu^I–S bonds. As a result the $Ag^I{}_8$ cube has longer edges than the $Cu^I{}_8$ cube. The Ni^{II}–S and Ni^{II}–N disances are shorter than the corresponding Cu^{II}–S and Cu^{II}–N bonds. Several structures of silver–sulfur cages with other thiolates have been reported. In $Ag_5(\mu\text{-}SC_6H_5)_7{}^{2-}$ the silver atoms do not occupy the apices of a regular polyhedron.[12a] The absence of a central halide ion allows shorter Ag^I–Ag^I distances (≥2.936 (1) Å) than in the present structure. The same is true for the distorted Ag_6 octahedron in $[AgS_2CN(C_3H_7)_2]_6$ wherein a short Ag^I–Ag^I distance of 2.905 (5) Å is present.[12b]

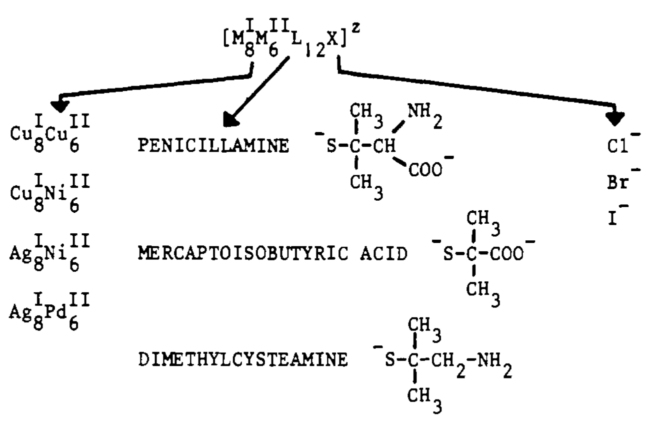

Figure 3. The compositions of the $[M^I{}_8M^{II}{}_6L_{12}Cl]^z$ anions. Complex cluster anions of this composition are known with different metals (this work), different ligands,[3-5] and different central halide ions.[3b]

Discussion

Stability of the Structure. There is a growing family of compounds, which are structurally related to the title compound, containing a variety of metals, ligands, and central halide ions. The combinations known thus far are shown in Figure 3. There are several structural features that seem to contribute to the stability of this configuration of metals and ligands. The arrangement of sulfur atoms is such that suitable coordination geometries are obtained for the univalent as well as the bivalent metal ions. The sulfur atoms function as bridges between the metal ions so that each sulfur atom is in a tetrahedral environment of one carbon atom, two univalent

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(12) (a) Dance, I. G. *Aust. J. Chem.* **1978**, *31*, 2195. (b) Hesse, R.; Nilson, L. *Acta Chem. Scand.* **1969**, *23*, 825.

metal atoms, and one divalent metal atom and that a stable sp^3 hybridization at the sulfur atom is realized. The ligands form five-membered chelate rings around the divalent metal. Apparently a similar structure cannot be stabilized by the formation of six-membered chelate rings. *N*-acetylpenicillamine can form six-membered chelate rings via S and O atoms, but no stable mixed-valence compound analogous to $[Cu^I{}_8Cu^{II}{}_6(MIBA)_{12}Cl]^{5-}$ can be synthesized.[13] The 24 methyl substituents on the carbon atoms adjacent to sulfur protect the univalent metals sterically against oxidation (Cu^I; see ref 3b) or chemical attack (e.g., of Ag^I by Cl^-).

Chromatographic analysis on Sephadex G-25 proved that the $[Cu^I{}_8Cu^{II}{}_6Pen_{12}Cl]^{5-}$ structure remains intact in solution.[14] We observed that $[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl]^{5-}$ behaves identically on Sephadex G-25, indicating that this structure also is stable in aqueous soltuion.

Structure of $Na_5Cu^I{}_8Ni_{10}(Pen)_{16}Cl\cdot{\sim}31H_2O$. This insoluble compound precipitates in the preparation of $Na_5[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl]\cdot{\sim}40H_2O$ if only a small volume of the buffer solution is used. The only difference in the infrared spectra of these compounds (4000–200 cm^{-1}) is a shift in the carboxylate stretching frequency. The magnetic susceptibility of this compound is compatible with the presence of four paramagnetic ($S = 1$) Ni^{II} atoms in the complex ion (Table I). We postulate that the central diamagnetic $[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl]^{5-}$ core is also present in this structure and that 4 additional paramagnetic Ni^{II} atoms are bound by the 12 carboxylate groups at the surface of the cluster. Each additional Ni^{II} atom is then octahedrally coordinated by three carboxylate groups of the central cluster and an additional tridentate penicillaminato ligand.[15] When only a small amount of buffer is used, the reduction reaction

$$2Cu^{2+} + HSC(CH_3)_2CH(NH_3^+)COO^- \rightarrow 2Cu^+ + [SC(CH_3)_2CH(NH_3^+)COO^-]_2 + 2H^+$$

cannot be complete; the theoretical amount of $[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl]^{5-}$ is not formed, and excess Ni^{II} and H_2Pen are available for binding at the surface of the cluster. The random orientations of the four penicillaminato ligands at the surface of the $[[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl][NiPen]_4]^{5-}$ ions make it unlikely that this compound will ever be crystallized.

Spectral and Magnetic Properties. Only the octahedrally coordinated Ni^{II} atoms and square-planar coordinated Cu^{II} atoms in these cluster compounds are paramagnetic. The paramagnetism of the Cu^{II}-containing complexes has been studied in detail.[5b,6] There is a ferromagnetic exchange interaction between the six Cu^{II} atoms so that the magnetic ground state is characterized by the spin quantum number $S = 3$. The ESR spectra of the $[Cu^I{}_8Cu^{II}{}_6L_{12}Cl]^{5-}$ compounds, where L = Pen or DMC, are unresolved.[4b,5b] Only a broad absorption around $g = 2$ is observed in frozen solution. The intramolecular Cu^{II}–Cu^{II} interactions obviously broaden the signal. It is possible, however, to obtain well-resolved ESR spectra from Cu^{II} in these cluster compounds after magnetic dilution in the $Ag^I{}_8Ni^{II}{}_6$- or $Cu^I{}_8Ni^{II}{}_6$-containing compounds. In fact the $Cu^I{}_8Ni^{II}{}_6$ derivative is always weakly paramagnetic and produces a well-resolved ESR spectrum. Apparently small amounts of Cu^{II} are present at the Ni^{II} sites. No separate visible absorption at 518 nm (as in the $Cu^I{}_8Cu^{II}{}_6$-containing compounds) is present although a weak shoulder at this wavelength on a broad UV absorption tailing in the visible spectrum is observed in some samples. A Cu^{II}-doped sample of $[Ag^I{}_8Ni^{II}{}_6Pen_{12}Cl]^{5-}$ was prepared by using the method used for the pure compound replacing 10% of the amount of $NiCl_2\cdot 6H_2O$ by a corresponding amount of $CuCl_2\cdot 2H_2O$. The ESR spectra of both the Cu^{II}-doped $Ag^I{}_8Ni^{II}{}_6$ compound and the $Cu^I{}_8Ni^{II}{}_6$ cluster in frozen aqueous solution (77 K) are almost identical ($g_\perp = 2.02$, $g_\parallel = 2.14$, $A_\parallel = 167 \times 10^{-4}$ cm^{-1} and $g_\perp = 2.02$, $g_\parallel = 2.12$, $A_\parallel = 168 \times 10^{-4}$ cm^{-1}, respectively). This observation of ESR spectra, typical for Cu^{II}, square-planar coordinated by a N_2S_2-donor set also proves that the unpaired electron remains localized on the Cu^{II} atom as no additional hyperfine splitting due to other Cu^I or Ag^I atoms is observed. The model employed to calculate the ferromagnetic exchange interactions in the $Cu^I{}_8Cu^{II}{}_6$ cluster compounds[5b,6] is based on an octahedral arrangement of isolated spins. The present ESR spectra are an additional justification for this model.

Registry No. $[Co(NH_3)_6]_5[Ag^I{}_8Ni^{II}{}_6Pen_{12}Cl]_3\cdot xH_2O$, 78167-29-0; $[Co(NH_3)_6]_5[Ag^I{}_8Pd^{II}{}_6Pen_{12}Cl]_3$, 78167-30-3; $Na_5[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl][Ni^{II}Pen]_4$, 78003-74-4; $Na_5[Cu^I{}_8Ni^{II}{}_6Pen_{12}Cl]$, 78003-75-5; $Na_5[Cu^I{}_8Cu^{II}{}_6Pen_{12}Cl]$, 65028-63-9.

Supplementary Material Available: Listings of observed and calculated structure factors and calculated positions for hydrogen atoms (9 pages). Ordering information is given on any current masthead page.

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(13) Sugiura, Y.; Tanaka, H. *Chem. Pharm. Bull.* **1970**, *18*, 368.

(14) Wright, J. R.; Frieden, E. *Bioinorg. Chem.* **1975**, *4*, 163.

(15) Model-building studies show that this is indeed possible without any strain in the complex ion. The four additional Ni^{II} atoms occupy the apices of a tetrahedron, a fourth regular polyhedron in the structure.