Polynuclear Mixed-metal Thiolate Complexes with D-Penicillamine

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Summary Diamagnetic cluster-compounds of composition $[M^I_8M^{II}_6\{SC(Me)_2CH(NH_2)CO_2\}_{12}Cl]^{5-}$ with $M^I_8M^{II}_6$ = $Cu^I_8Ni^{II}_6$, $Ag^I_8Ni^{II}_6$, and $Ag^I_8Pd^{II}_6$ are structually related to the well characterized $Cu^I_8\,Cu^{II}_6$ compound so that the M^I atoms are trigonally co-ordinated by 3 sulphur atoms and the M^{II} atoms are planar 4-co-ordinated by 2 sulphur and 2 nitrogen atoms

D-PENICILLAMINE $[HSC(Me)_2CH(NH_2)CO_2H]$ promotes the urinary excretion of copper in patients with Wilson's disease It was shown[1] that under simulated physiological conditions D-penicillamine and copper form a polynuclear, anionic, mixed-valence Cu^ICu^{II}-complex An *X*-ray structure determination revealed that the composition of this compound is $[Cu^I_8Cu^{II}_6L_{12}Cl]^{5-}$, where L is the deprotonated penicillamine ligand $[^-SC(Me)_2CH(NH_2)CO_2^-]$ (pen) (schematic structure shown in the Figure)

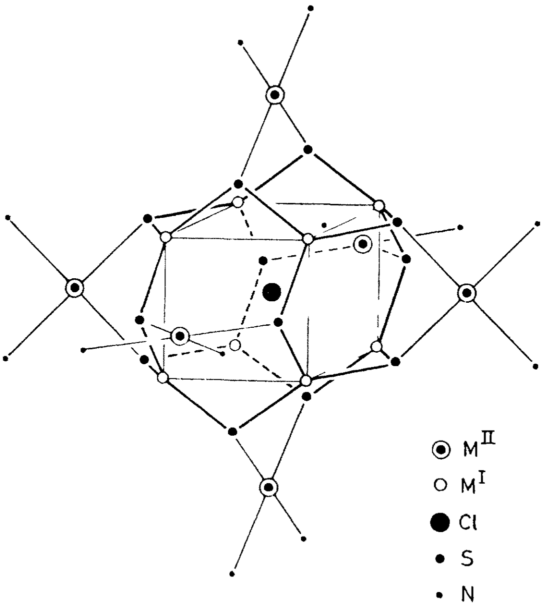

FIGURE Structure of the mixed-metal D penicillamine compounds Only the $[M^I_8M^{II}_6S_{12}N_{12}Cl]$ core of the complex anions is shown A complete drawing of the $[Cu^I_8Cu^{II}_6L_{12}Cl]^{5-}$ ion is in ref 1

We report here the existence of similar complexes of D-penicillamine with metals other than copper and with combinations of different metals (Table) Crystalline derivatives of these compounds have been obtained with $Co(NH_3)_6^{3+}$ as the counter-ion Satisfactory analyses (M^I,M^{II},C,H,Co,Cl,N,S) were obtained for the $Co(NH_3)_6^{3+}$ or Na^+ salts of the complexes The cluster compound $[Co(NH_3)_6]_5[Ag^I_8Ni^{II}_6L_{12}Cl]_3$*ca* $197H_2O$ crystallizes in the cubic space group F432 with *a* 51 77(1) Å The Tl^+ salt of the analogous Cu^ICu^{II} compound crystallizes in the same space group with *a* 50 847(5) Å The structure consists of ordered, complex ions interlinked by hydrogen bonds and disordered Tl^+ ions and water molecules[1] Most likely the novel $Ag^I_8Ni^{II}_6$ cluster compound has an analogous structure containing disordered $Co(NH_3)_6^{3+}$ ions and water molecules The complete *X*-ray structure of the latter compound is under investigation

The $Ag^I_8Ni^{II}_6$ and $Ag^I_8Pd^{II}_6$ containing compounds are diamagnetic (n m r) Different samples of the $Cu^I_8Ni^{II}_6$ complex show varying degrees of weak paramagnetism, most likely due to the presence of some Cu^{II} in the Ni^{II} sites The e s r spectrum at 77 K of this latter compound in frozen aqueous solution shows that Cu^{II} is in an approximately axially symmetric environment with parameters ($g_\perp$ 2 02, $g_\parallel$ 2 12, $A_\parallel$ 168 × 10^{-4} cm^{-1}) similar to those of a Cu^{II}-doped sample of $[Ag^I_8Ni^{II}_6(pen)_{12}Cl]^{5-}$ ($g_\perp$ 2 02, $g_\parallel$ 2 14, $A_\parallel$ 167 × 10^{-4} cm^{-1}) The e s r spectra thus indicate that Cu^{II} is planar co-ordinated and that the unpaired electron appears to be mainly localized on a single Cu^{II} atom, as no additional hyperfine splitting of other Cu atoms is observed This observation is an additional justification of the model employed to calculate the ferromagnetic exchange interactions in the $Cu^I_8Cu^{II}_6$ cluster compounds with D-penicillamine and related ligands,[2,3] as this model is based on an octahedral arrangement of 6 isolated spins with S $\frac{1}{2}$

The compounds are prepared in 0 2 M sodium acetate buffer (pH 6) from stoicheiometric quantities of D-penicillamine and salts of the constituent metal salts (these must include a chloride as chloride is essential for the formation of these compounds) In a typical preparation 450 mg of D-penicillamine (3 mmol) was dissolved in 60 ml of 0 2 M sodium acetate buffer A solution of 340 mg of $AgNO_3$ (2 mmol) in a few ml of water was added to this solution, followed by a solution of 355 mg of $NiCl_2$ $6H_2O$ (1 5 mmol) in

TABLE N m r and visible spectra of $[M^I_8M^{II}_6\{SC(Me)_2CH(NH_2)CO_2\}_{12}Cl]^{5-}$ compounds

		Visible spectrum[a]		N m r spectrum[b]		
M^IM^{II}	Colour	ν_{max} cm^{-1}	$\epsilon/dm^3\,mol^{-1}\,cm^{-1}$	α-CH	Me	Me
Cu^ICu^{II}	Purple	19 300	25 500			
Cu^INi^{II}	Brown	—[c]				
Ag^INi^{II}	Red	21 700[d]	1 050[e]	3 96	2 58	1 79
Ag^IPd^{II}	Yellow	—[c]		3 37	2 25	1 63

[a] Measured in 0 2 M aqueous sodium acetate buffer [b] Measured in D_2O at 99 5 MHz with reference TSP $[(Me)_3SiCD_2CD_2CO_2Na]$ [c] No absorption maxima in the visible region (below 27 000 cm^{-1}) A tail from an intense absorption in the u v region possibly obscures the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition expected at *ca* 21 000 cm^{-1} for square planar co ordinated Ni^{II} [d] This band can be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition mentioned above [e] This band lies on the slope of an intense absorption in the u v region The value of ε may therefore be exaggerated

6 ml of water. The resulting red solution was treated with ethanol and a red, gelatinous precipitate of the hydrated Na^+ salt of $[Ag_8Ni_6L_{12}Cl]^{5-}$ was obtained. It was filtered off and washed with alcohol and ether. Crystals of the $Co(NH_3)_6^{3+}$ salt of this compound can be obtained as described for the parent $Cu^{I}_{8}Cu^{II}_{6}$ complex.[1]

We thank Professor J. Reedijk for stimulating discussions.

(*Received*, **16*th*** *June* 1980; *Com*. 652.)

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