Inorganica Chimica Acta, 25 (1977) L11–L14

Synthesis, Structure, and Resonance Raman Spectra of Some Copper–Sulfur Atom Clusters

O. SIIMAN

Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676, U.S.A.

C. P. HUBER and M. L. POST

Division of Biological Sciences, National Research Council of Canada, Ottawa, Ontario, Canada

Received August 8, 1977

Recent interest in Cu(I)–sulfur ligand clusters has revealed several basic structures: (1) the $Cu_8^IS_{12}$, Cu_8 cube, S_{12} icosahedron core with 1,1-dicyanoethylene-2,2-dithiolate [1], 1,2-dithiosquarate [2], penicillamine [3], and β,β-dimethylcysteamine [4]; (2) the $Cu_4^IS_6$, Cu_4 tetrahedron, S_6 octahedron core with thiourea [5] and benzenethiolate [6]; (3) the $Cu_4^IS_8$, Cu_4 tetrahedron, two S_4 tetrahedra core with diethyldithiocarbamate [7]. Oxidation of these tetranuclear and octanuclear Cu(I) clusters to produce mixed valence Cu (I, II) clusters has not been reported. Herein, we report the preparation of several copper clusters [Cu_3L_4 (**I**), its dissociation product, Cu_3L_3 (**II**), and a chlorinated species $[Cu_4L_3][CuCl_2]CCl_4$ (**III**), where L represents the bidentate tetraphenyldithioimidodiphosphinate [8] ligand, $(-S-P(C_6H_5)_2-N-P(C_6H_5)_2)-S-^{-})$], the single X-ray structure of **III**, the first example of a $Cu_4^IS_6$ core with a bidentate sulfur ligand, and the resonance Raman (RR) [9] spectrum of the mixed valence compound, **I**.

Reaction between NaL and $CuCl_2$ in aqeuous solution precipitated a dark purple compound, **I**, which was further purified in toluene by gel permeation chromatography (Bio-beads SX-2). Colorless crystals of **II**, mp 223–4 °C, were obtained from toluene solution of the initial fraction when aged (> 24 hr) solutions of **I** were chromatographed on the same gel column. The trailing yellow fraction contained the oxidized ligand, HL′, $HO-P(C_6H_5)_2-N-P(C_6H_5)_2-S$ and elemental sulfur. Work-up of **I** in $CCl_4-CH_2Cl_2$ solutions yielded pale pink crystals of **III**. Satisfactory analyses were obtained.

Magnetic susceptibility measurements show that **I** has a magnetic moment, μ_{eff} = 1.90 B.M., and **II** and **III** are diamagnetic. Crystals of **III** have monoclinic symmetry, space group $P2_1/c$, and cell parameters a = 11.417(9), b = 37.904(3), c = 20.622(14) Å, β = 116.18(5)°, D_m = 1.562 g cm^{-3}, Z = 4, D_c = 1.565 g cm^{-3}. Three-dimensional intensity data were collected with a Picker card-controlled diffractometer using Ni-filtered Cu radiation. The structure was solved by a combination of direct and heavy-atom methods, and refined by block-diagonal least-squares to a conventional R value of 0.081.

The crystal structure is composed of discrete $Cu_4(C_{24}H_{20}NP_2S_2)_3^+$ cations, dichlorocuprate(I) anions, and carbon tetrachloride solvent molecules. The tetrahedrally-arranged clusters of four Cu(I) atoms are surrounded by three bidentate ligands as shown in Fig. 1. Each of the coordinating sulfur atoms bridges two copper atoms, while each copper is coordinated by three sulfur atoms, giving a Cu_4S_6 core arrangement similar to that previously found [5, 6]. In the present structure three copper atoms are chemically equivalent, being coordinated by both ends of a single ligand and by one end of another ligand, while the fourth copper atom of each cation is different, being coordinated by three different ligands. The crystal structure reflects this; an approximate (non-crystallographic) 3-fold symmetry axis passes through the unique copper atom of each cation and through the mid-point of the other three copper atoms. One of the phenyl groups, however, is twisted about 55° out of the symmetric orientation in order to accommodate the carbon tetrachloride molecule. Each of the four Cu(I) atoms in the cation is nearly coplanar with its three coordinating sulfur atoms; the deviations of the copper atoms from the planes defined by the surrounding sulfur atoms are 0.12, 0.12, 0.11, and 0.09 Å. The six-membered rings formed by each of the ligands with a copper atom are in flattened chair conformation. An earlier structure [11] of $Mn(II)L_2$ showed the chelate rings in twisted boat conformation.

Average bond distances and angles and their root-mean-square deviations are (1) in the Cu_4S_6 cage: Cu–S, 2.266(6); S–Cu–S, 119.3(1.0); Cu–S–Cu, 76.0(0.3); and (2) in the chelate rings: S–P, 2.053(8); P–N, 1.579(15); P–C, 1.799(9); C–C, 1.379 Å (31); Cu–S–P, 101.7(0.3); S–P–N, 118.2(0.4); S–P–C, 106.7(0.3); N–P–C, 108.8(0.9); C–P–C, 107.2 (0.4); S–Cu–S, 121.0° (2.7). The occurrence of the dichlorocuprate(I) ion was first established only in 1970 [12]. In the present structure the very large thermal vibration of the $CuCl_2^-$ group precludes accurate bond length measurement, but the Cu–Cl distances found here, 1.96 and 2.09 Å, and the Cl–Cu–Cl angle, 177°, are at least similar to the few values available for comparison [12–14].

The electronic absorption spectrum of **I** exhibits bands ($\epsilon \sim 500\ M^{-1}$ cm^{-1}) centered at 585 and 410 nm. No additional near-infrared bands were observed. Laser excitation into the 588 nm absorption band of a solid sample gave Raman spectra (Figure 2) in which several resonance-enhanced bands between 900 and 200 cm^{-1} were detected. In particular, when the phenyl ring vibrational mode at 1596 or 1000 cm^{-1} is adopted as an internal standard, an excitation

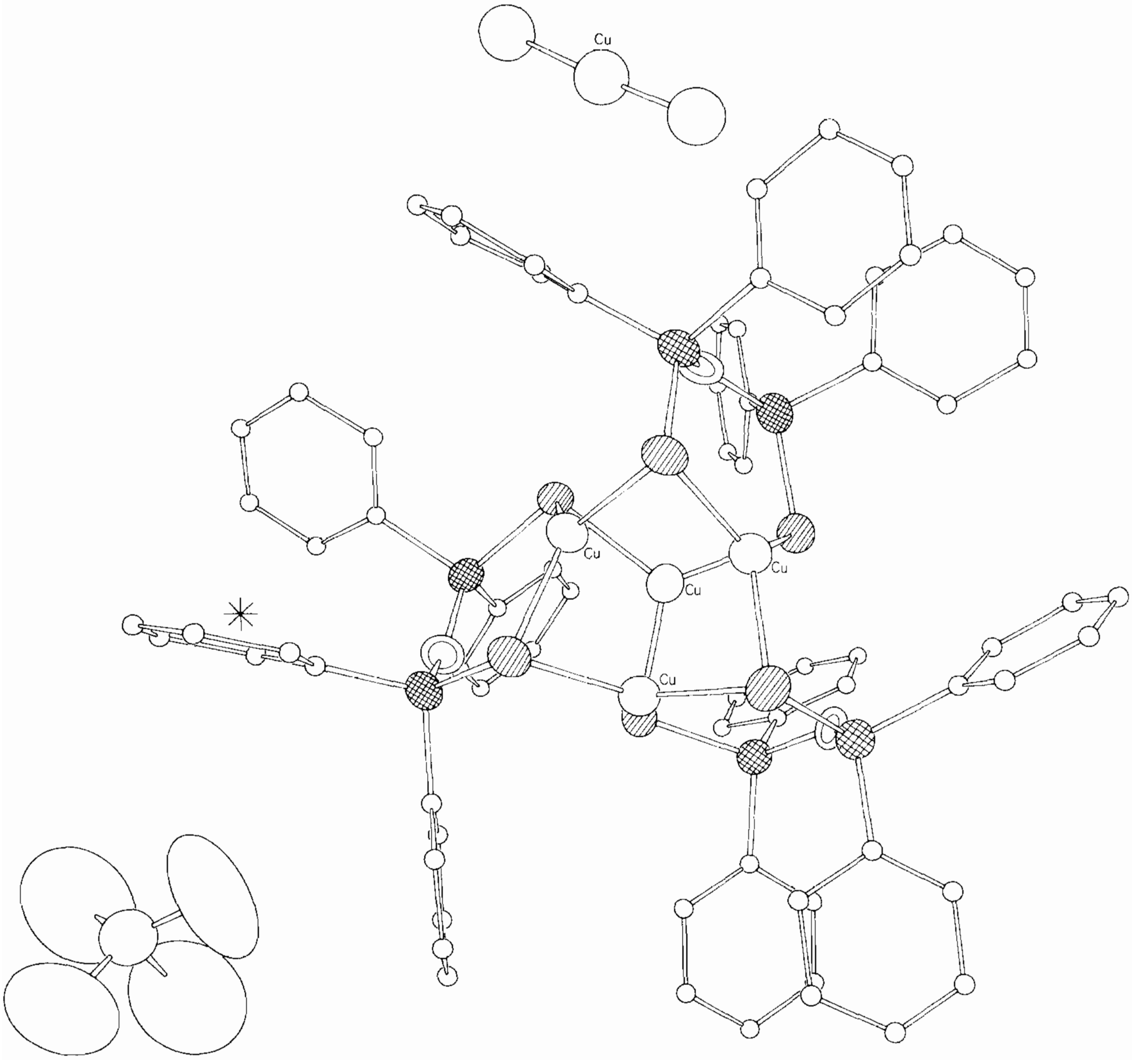

Fig. 1. An ORTEP [15] drawing of an asymmetric unit of $Cu_4(C_{24}H_{20}NP_2S_2)_3^+ \cdot CuCl_2^- \cdot CCl_4$. The viewing direction is almost parallel to the approximate 3-fold axis; the phenyl ring marked with an asterisk is rotated by about 55° from the symmetric orientation. The phenyl carbon atoms are shown as spheres of arbitrarily small radius for clarity; the outlines of the other atoms enclose 50% probability. Sulfur atoms are striped, phosphorus atoms are cross-hatched, and nitrogen is shown with double circles.

TABLE I

λ_0 (nm)	F_A^2	Observed relative intensities	
		1596 cm^{-1}	1000 cm^{-1}
647.1	26	33	14
568.2	4900	140	26
530.9	46	41	21
514.5	16	14	8
488.0	5	4	3
441.6	1	1	1

profile for the 820 cm^{-1} RR band can be deduced. Calculated enhancement factors [16] (F_A^2) (Table I) relative to 441.6 nm Cd excitation agree with observed intensities and show that the 820 cm^{-1} vibrational mode is resonance-enhanced by coupling to a single electronic transition whose absorption maximum lies at 585 nm. The 820 cm^{-1} band is not present in the IR spectrum of **I** and occurs weakly in its normal Raman spectrum (441.6 nm excitation). IR spectra of **I** show that all sulfur atoms are coordinated ($\nu(P\underline{\cdots}S)$ [8a] is found below 600 cm^{-1}) and that nitrogen is not coordinated (only one intense broad band at 1220 cm^{-1}, ν_{as}(PNP) [8a] is observed). Since normal coordinate analysis of a 1:1 CuL model with C_2 symmetry indicated that ν_s(PNP) should appear in the 800–900 cm^{-1} region, the 820 cm^{-1} RR band is tentatively assigned to ν_s (PNP).

Inspection of the adamantane-like Cu_4S_6 core structure of **III** suggests that removal of the unique

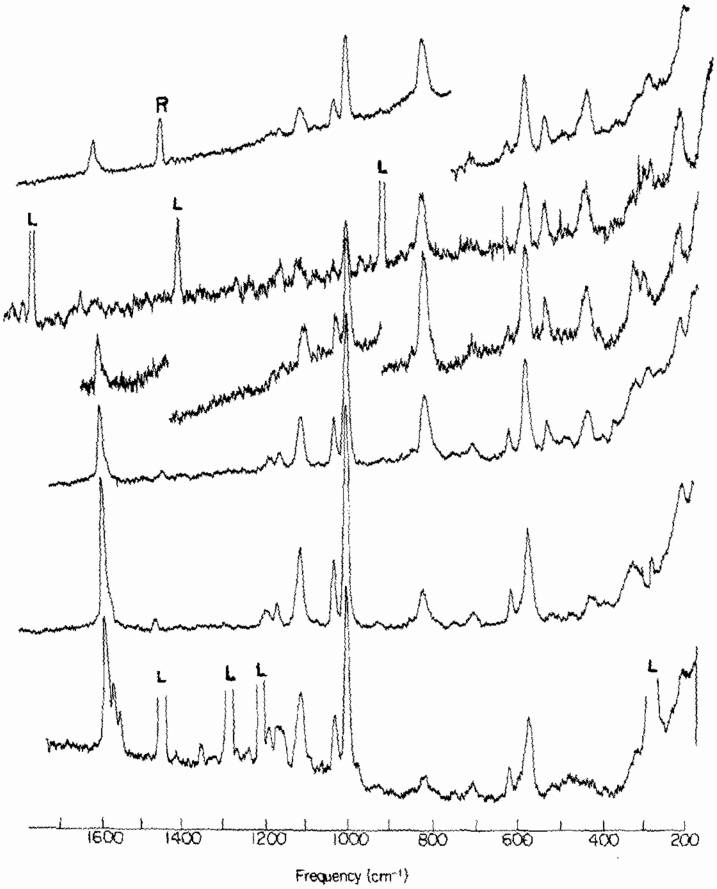

Fig. 2. Resonance Raman spectra of a solid sample (rotating cell) of $Cu_3(C_{24}H_{20}NP_2S_2)_4$. Experimental conditions: scan rate, 30 cm^{-1}/min.

	Excitation nm	Power mW	Slit width cm^{-1}	Sensitivity cps	Time constant sec
A (top)	647.1, Kr^+	300	8.6	1000	5
B	568.2, Kr^+	60	10	800	2
C	530.9, Kr^+	30	10	800	2
D	514.5, Ar^+	250	8.7	1000	5
E	488.0, Ar^+	260	8.6	1000	5
F (bottom)	441.6, Cd	75	6.9	1000	2

L, plasma lines; R, grating ghost

Cu(I) would give rise to Cu_3S_3 ring core structures for **II** and **I**. The μ_{eff} value for **I** shows the presence on the average of one Cu(II) site and two Cu(I) sites. In ML_2 complexes [8b, 11] as well as in $Cu^{II}L'_2$ [17] the spectral region below 25,000 cm^{-1} is void of any intense absorption bands that could be assigned to M → L or L → M charge transfer transitions; therefore, the 585 nm electronic absorption band of **I** is provisionally assigned to Cu(I) → Cu(II) intervalence charge transfer. The absence of low-energy Cu(II) ligand field bands makes **I** a Class III [18] mixed valence complex. For low-energy charge transfer the geometry of both metal sites should be similar (probably distorted tetrahedra) to avoid large bond reorganization energies and the sites should be flexible (a large Stokes shift in the electronic emission spectrum [19] of MnL_2 implied flexibility in metal sites with this sulfur ligand).

Acknowledgments

This work was supported in part at Clarkson College by the National Institutes of Health (Grant GM-23072). We thank Dr. P. R. Carey for use of the Jarrell-Ash 25-100 Raman spectrometer in the RR spectral measurements.

References

1 L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler and K. Knox, *J. Am. Chem. Soc., 90,* 7357 (1968).

2 F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc., 96,* 5646 (1974).

3 P. J. M. W. L. Birker and H. C. Freeman, *Chem. Comm.,* 312 (1976).

4 H. J. Schugar, C. Ou, J. A. Thich, J. A. Potenza, R. A. Lalancette, and W. Furey, Jr., *J. Am. Chem. Soc., 98,* 3047 (1976).

5 E. H. Griffith, G. W. Hunt, and E. L. Amma, *Chem. Comm.,* 432 (1976).

6 I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta, 19,* L41 (1976).

7 R. Hesse, *Ark. Kemi, 20,* 481 (1963).

8 (a) A. Schmidpeter and H. Groeger, *Z. Anorg. Allg. Chem., 345,* 106 (1966); (b) A. Davison and E. S. Switkes, *Inorg. Chem., 10,* 837 (1971).

9 J. Behringer, *Raman Spectrosc., 1,* 168 (1967).

10 A. Schmidpeter and H. Groeger, *Chem. Ber., 100,* 3979 (1967).

11 O. Siiman and H. B. Gray, *Inorg. Chem., 13,* 1185 (1974).

12 (a) M. G. Newton, H. D. Caughman, and R. C. Taylor, *Chem. Comm.,* 1227 (1970); (b) M. G. Newton, H. D. Caughman and R. C. Taylor, *J. Chem. Soc. Dalton,* 258 (1974).

13 W. C. Marsh and J. Trotter, *J. Chem. Soc. (A),* 1482 (1971).

14 J. Kaiser, G. Brauer, F. A. Schroder, I. F. Taylor, and S. E. Rasmussen, *J. Chem. Soc. Dalton,* 1490 (1974).

15 C. K. Johnson, ORTEP, Report ORNL-3794 (2nd rev.), Oak Ridge National Laboratory, Oak Ridge, Tennessee (1970).

16 A. C. Albrecht and M. C. Hutley, *J. Chem. Phys., 55,* 4438 (1971).

17 O. Siiman, unpublished results.

18 H. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem., 10,* 247 (1967).

19 O. Siiman, M. Wrighton and H. B. Gray, *J. Coord. Chem., 2,* 159 (1972).

Appendix

Analyses

Compound **I**: *Anal.* Calcd for $Cu_3(C_{24}H_{20}NP_2S_2)_4$: C, 58.10; H, 4.06; N, 2.82; S, 12.93; P, 12.49; Cu, 9.60%; M.W. 1985. Found: C, 60.53; H, 4.52; N, 2.96; S, 12.35; P, 11.80; Cu, 9.25%; dissociates in benzene, M.W. (0.005 *M* benzene), 1095.

Compound **II**: *Anal.* Calcd for $Cu_3(C_{24}H_{20}NP_2S_2)_3$: C, 56.30; H, 3.94; N, 2.74; Cu, 12.41%; M.W. 1536. Found: C, 56.76; H, 4.07; N, 2.68; Cu, 12.63%; M.W. (benzene), 1566.

Compound **III**: *Anal.* Calcd for $[Cu_4(C_{24}H_{20}NP_2S_2)_3][CuCl_2]CCl_4$: C, 46.44; H, 3.20; N, 2.23; S, 10.19; Cu, 16.83%; M.W. 1888. Found: C, 47.30; H, 3.20; N, 2,21; S, 10.06; Cu, 16.39%; M.W. (benzene), 1800.