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X-ray Crystal Structure of Bis(N,N′-ethylene-bis-(salicylideneiminato)-Oxovanadium(V)) Di-μ-chloro-dicopper(I) Chloride, a Compound with a Three-Coordinate Copper(I) Chloride

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The chemistry of copper(I) complexes has gained much interest in the last few years [2], mainly because of their catalytic properties. The copper(I) ions can be found in several different stereochemistries among which tricoordination is by no means uncommon [2, 3]. However, simple tricoordinated copper(I) halides have never been reported. In solution linear $CuCl_2^-$ species were described [4] while in the solid polymeric tetrahedral species are more common [2]. Even compounds which stoichiometrically contain $CuCl_3$ units are known to contain tetrahedral species [5]. We wish to report here the X-ray structure characterization of a novel dinuclear $Cu_2Cl_4^{2-}$ species which is the first example of a tricoordinated copper(I) halide.

Tetradentate Schiff bases derived from salicylaldehyde are known to act as bidentate ligands towards metal ions, yielding binuclear and trinuclear complexes [6]. In particular Cu(SALen) (SALen is the Schiff base formed from salicylaldehyde and 1,2-diaminoethane) has been reported to react with $NiCl_2$ and $CoCl_2$ yielding complexes of formula $Cu(SALen)MCl_2$. In an attempt to prepare the analogous oxovanadium(IV) derivative, by reacting Cu(SALen) with $VOCl_2$ in chloroform/ethanol mixtures we obtained a dark-brown crystalline material which analyzed satisfactorily for $Cu(SALen)VOCl_2 \cdot H_2O$. Room temperature magnetic susceptibility measurements showed that the compound was diamagnetic. This result was unexpected since, although a fairly strong antiferromagnetic coupling between copper(II) and oxovanadium(IV) was claimed in one case [7], in the only fully-characterized example copper(II) and oxovanadium(IV) turned out to be ferromagnetically-coupled [8].

With the aim of understanding the origin of the diamagnetism of the complex we determined its crystal structure through X-ray diffraction [9].

From the X-ray results it turned out that the compound was incorrectly formulated in the sense that the VO group is bound to SALen, while the copper ion is bound to chloride. In the unit cell are contained two $VO(SALen)H_2O$ species, and one centrosymmetric Cu_2Cl_4 species. The only way of explaining these data is to assume that a redox process occurred whereby VO(IV) was oxidized to VO(V) and Cu(II) reduced to Cu(I). Therefore the compound must be correctly formulated as $VO(SALen)H_2O_2Cu_2Cl_4$. The two ions are shown in Figs. 1 and 2. The same compound is obtained when VO(SALen) is reacted with $CuCl_2$ in chloroform/ethanol mixtures. A similar redox process occurs when VOSALen is reacted with $CuBr_2$ under analogous conditions. Similar reactions were observed also using different tetradentate Schiff bases.

V–O1 = 1.827(5), V–O2 = 1.810(5), V–O3 = 1.590(5), V–O4 = 2.310(5), V–N1 = 2.073(6), V–N2 = 2.083(6), O2–V–O1 = 107.1(2), N1–V–O1 = 86.3(2), N1–V–N2 = 76.4(3)

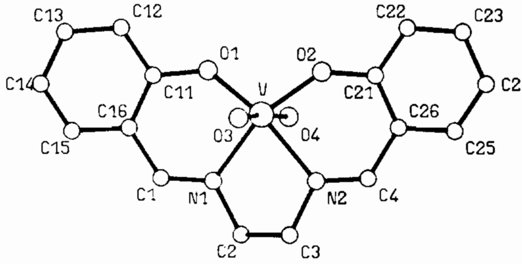

Fig. 1. Perspective drawing of the cation $VO(V)SALen^+$, showing selected bond distances (Å) and angles (Deg) around the metal atom.

CU–CL1 = 2.161(2), CU–CL2 = 2.224(3), CU–CL2* = 2.427(3), CL1–CU–CL2 = 143.9(1), CL2–CU–CL2* = 96.8(2)

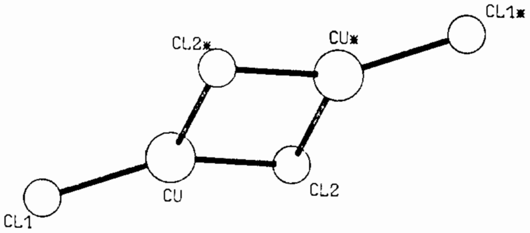

Fig. 2. Perspective view of the anion $Cu_2Cl_4^{2-}$ showing selected bond distances (Å) and angles (Deg). The atoms labelled with * are referred to the corresponding unlabelled ones by an inversion center.

The $Cu_2Cl_4^{2-}$ ion is completely planar. The bridge is rather asymmetric, with one Cu–Cl distance much larger than the other (2.427(3) *vs.* 2.224(3) Å), while the shortest Cu–Cl bond is that with the terminal chloride atom (2.161(2) Å). The bonds lengths of the bridge chlorides compare well with those reported for other similar complexes [10, 11].

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The bond angles are also rather asymmetric, with a Cl_2–Cu–Cl_2* angle of 96.8(2)° and a Cl_2–Cu–Cl_1 angle of 143.9(1)°. No other contacts of the copper(I) ion below 2.94 Å are present in the cell.

The V=O distance is 1.59 Å, which is not significantly different from those reported for oxovanadium(IV) complexes [12, 13]. Much larger differences from the values reported for oxovanadium(IV) complexes are observed in the equatorial bond distances; the V–O distances are much shorter than those observed in VO(IV)SALen (1.82 Å on the average *vs.* 1.92 Å) while the V–N distances are longer (2.08 *vs.* 2.07 Å). The vanadium atom is 0.27 Å above the N_2O_2 plane, the mean deviation of the latter atoms being 0.064 Å. The water molecule which completes the coordination polyhedron is at 2.310 Å from the vanadium atom. The differences between $VO(SALen)H_2O^+$ and VO(SALen) can be rotationalized taking into account the harder character of vanadium(V) as compared to V(IV), which gives shorter V–O and longer V–N bond distances.

References

1 (a) Department of Chemistry; (b) I.S.S.E.C.C.; C.N.R.

2 F. H. Jardine, *Adv. Inorg. Chem. Radiochem., 17,* 116 (1975).

3 P. G. Eller, D. G. Bradley, M. B. Hursthouse and D. W. Meek, *Coord. Chem. Rev., 24,* 1 (1977).

4 J. A. Creighton and E. R. Lippincat, *J. Chem. Soc. London,* 5314 (1963); D. H. Waters and B. Basak, *J. Chem. Soc. A,* 2733 (1971).

5 C. Brink and C. H. MacGillary, *Acta Cryst., 2,* 158 (1949).

6 E. Sinn and C. M. Harris, *Coord. Chem. Rev., 4,* 391 (1969).

7 D. E. Fenton and S. E. Gayda, *J.C.S. Dalton,* 2109 (1977).

8 O. Kahn, P. Tola, J. Galy and H. Coudanne, *J. Am. Chem. Soc., 100,* 3931 (1978).

9 Crystal and refinement data for $[VOSALenH_2O]_2Cu_2Cl_4$: $a = 9.759(3)$ Å, $b = 9.947(3)$ Å, $c = 10.115(3)$ Å, $\alpha = 108.73°(2)$, $\beta = 104.56°(2)$, $\gamma = 86.05°(2)$; space group $P1$; $Z = 2$, $d_{calcd} = 1.79$ g cm^{-3}; crystal dimensions (mm) 0.1 × 0.1 × 1.16; $\mu = 20.1$ cm^{-1}; data were collected using $\theta - 2\theta$ scan at a rate of 5° min^{-1} with $(1.00 + 0.30 \tan \theta)°$ scan width; $2.5° < \theta < 22°$ (Mo, $\lambda(K\alpha_1)$ 0.70926 Å); unique reflection collected 2215; reflection used in refinement, $F_o^2 > 3\sigma(F_o^2)$, 1358; parameters 235. All crystal data were collected on a Philips PW1100 four circle automated diffractometer. The structure was solved by direct method using the program MULTAN (1978) and by subsequent Fourier electron density maps. The structure was refined by full matrix least squares techniques, anisotropic temperature factors were employed for all the non-hydrogen atoms in the asymmetric unit. The H atoms were introduced in calculated positions [riding, C–H = 0.95 Å, U(H) 1.2-U(C)]. The final refinement gave $R = 0.044$.

10 M. R. Churchill and F. J. Rotella, *Inorg. Chem., 18,* 166 (1979).

11 J. A. Campbell, C. L. Raston and A. M. White, *Aust. J. Chem., 30,* 1937 (1977).

12 M. Pasquali, F. Marchetti, C. Floriani and M. Cesari, *Inorg. Chem., 19,* 1198 (1980).

13 M. Mathew, A. J. Carthy and G. J. Palenik, *J. Am. Chem. Soc., 92,* 3197 (1970).