Inorganica Chimica Acta, 18 (1976) L1 - L2
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

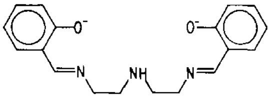
The Molecular Structure (X-ray Analysis) of the Copper(II) Compound of the Potentially Quinquedentate Ligand N,N′-bissalicylidene-1,5-diimino-3-azapentane

E. D. McKENZIE and S. J. SELVEY

Chemistry Department, The University, Sheffield S3 7HF, U.K.

Received January 2, 1975

As part of a continuing interest in the structures adopted by metal compounds with ligands that cannot readily fit any of the regular co-ordination polyhedra, we have been investigating the copper(II) compounds of the title ligand (I).



Although potentially a quinquedentate (as in the uranyl compound[1]), this ligand is unable to offer all of its potential donor atoms to a first-row transition metal in a mononuclear compound without gross strain.[2]

A green copper(II) compound of the ligand has been reported.[3,4] Our preparative study has been much more extensive and intensive, since we were looking for different structural types – including perhaps 'alcohol addition' compounds[5] which would allow quinquedentate behaviour of the modified ligand in a mononuclear compound. However, the molecular structure of the copper species appears to be the same in a whole series of different solvates which we have characterised. All are dark green 1:1 crystalline solvates, with no measurable differences in their diffuse reflectance electronic spectra (5,000–30,000 cm^{-1}) nor in their solution spectra. To define this molecular structure an X-ray analysis has been undertaken of one of the two characterised acetone solvates.

Dark green diamond-shapes plates were obtained from acetone.

Crystal data: $C_{36}H_{38}N_6O_4Cu_2\cdot2C_3H_6O$, M = 862.0; Monoclinic, a = 12.86(1), b = 16.74(2), c = 9.86(1), β = 105.1(1), Z = 2. Space group $P2_1/c$ [C^5_{2h}, No. 14].

X-ray data were collected on a Stöe Stadi-2 diffractometer (monochromated MoKα radiation) with stationary counter and moving crystal, giving 3555 independent reflections ($I > 3\sigma$).

The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares to a current R of 0.043. All non-hydrogen atoms have been allowed anisotropic vibrational parameters, and hydrogen atoms have been included but not refined.

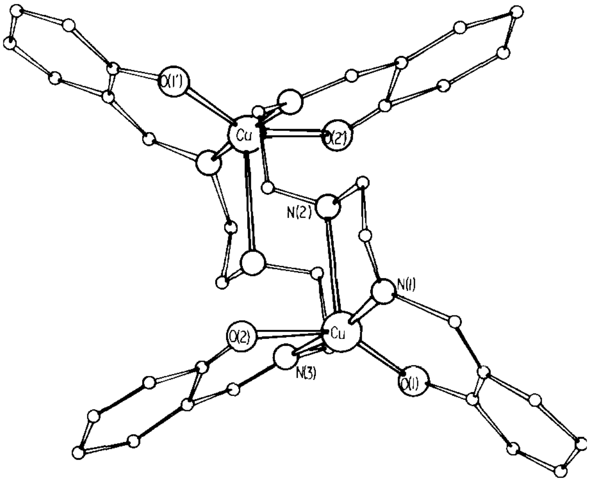


Figure. The centrosymmetric dimer.

The copper(II) compound, revealed by the analysis (Figure), is a centrosymmetric dimer [$Cu_2(L)_2$] in which each copper is five-coordinate, using three donors from one ligand, and two from the other. The salicylaldiminato moieties from the different ligands are bidentate to each copper [Cu–O(1) = 1.937(3); Cu–O(2) = 1.972(3); Cu–N(1) = 1.963(3); Cu–N(3) = 1.983(3) Å] and the fifth ligand is the secondary amine nitrogen at a rather longer distance of Cu–N(2) = 2.420(3) Å.

We prefer to describe the metal polyhedron as a distorted trigonal bipyramid, with N(1) and N(3) axial {N(1)–Cu–N(3) = 176.3(1)°} and O(1), O(2) and N(2) equatorial {O(1)–Cu–O(2) = 143.7(1)°; O(1)–Cu–N(2) = 125.1(1)°; O(2)–Cu–N(2) = 90.6(1)°}. However, N(2) is rather a long way from the ideal position for a 'regular' polyhedron {N(2)–Cu–N(1) = 77.2(1)°, and N(2)–Cu–N(3) = 100.1(1)°}. Such angular distortions appear to result largely, if not completely, from ligand constraints – the smaller of the last two angles quoted is internal to a chelate ring, whereas the larger is not.

Such dimers are formed without the major steric problems inherent in a monomer, and we have found no evidence for another species which might be the latter. A dimeric structure of this type would appear likely to be the generic one for compounds of related ligands, such as those reported by Lane and Taylor.[4] Much of the interpretation of the results of Taylor and co-workers[4,6] will need reassessment in the light of the structure reported here.

References

1 E. D. McKenzie, R. E. Paine and S. J. Selvey, *Inorg. Chim. Acta, 10,* 41 (1974); and references therein.

2 H. A. Goodwin in 'Chelating Agents and Metal Chelates', Ed. by F. P. Dwyer and D. P. Mellor, Academic Press, New York and London, 1964.

3 M. Augustin, H. J. Kerrinnes and W. Langenbeck, *J. prakt. Chem., 26,* 130 (1964).

4 L. W. Lane and L. T. Taylor, *J. Coord. Chem., 2,* 295 (1973).

5 C. M. Harris and E. D. McKenzie, *Nature, 196,* 670 (1962); C. M. Harris and E. D. McKenzie, *J. Chem. Soc. A,*746 (1969); M. Cressy, E. D. McKenzie and S. Yates, *J. Chem. Soc. A,* 2677 (1971).

6 L. T. Taylor and W. M. Coleman, *J. Am. Chem. Soc., 92,* 1449 (1971); L. T. Taylor and W. M. Coleman, *J. Inorg. Nucl. Chem., 33,* 3049 (1971); S. R. Edmondson, W. M. Coleman and L. T. Taylor, *Inorg. Chem., 12,* 1191 (1973); R. D. Patton and L. T. Taylor, *Inorg. Chim. Acta, 8,* 191 (1974).