Inorganica Chimica Acta, 15 (1975) L12
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The 6:1 Adduct of 4-Methylpyridine-1-oxide and Mercury(II) Perchlorate

J. F. VILLA

Department of Chemistry, H. H. Lehman College of CUNY, Bronx, New York 10468, U.S.A.

H. B. POWELL

Department of Chemistry, Eastern Kentucky University, Richmond, Kentucky 40475, U.S.A.

(Received July 21, 1975)

The chemistry of mercury(II) was expanded with the novel preparation by Carlin[1,2] of a 6:1 and a 2:1 oxo-adduct of pyridine-1-oxide and mercury(II). More recently Villa,[3] Pappas,[4] and Pappas, Villa and Powell[5] have reported the preparation and properties of a series of 6:1, 2:1 and 1:1 oxo-adducts of pyridine-1-oxide and mercury(II). Ahuja and Rostogi[6] have also reported some very similar compounds and in addition they have presented data on a few adducts with substituted pyridine-1-oxides, all of the 1:1 type. However, Carlin[2] reported the difficulties encountered when the preparation of the 6:1 adduct of 4-methylpyridine-1-oxide with mercury(II) was attempted. In fact, $[Hg(4\text{-}CH_3C_5H_4NO)_6](ClO_4)_2$ has eluded investigators so far, and only solids of indeterminate analysis have been obtained.[2] These difficulties with the parent compound of the 6:1 series have implied some kind of special interactions which sets this compound apart from the unsubstituted 6:1 pyridine-1-oxide complexes and apparently has stopped researchers in this area for the last few years. We have now successfully prepared this compound and measured its physical properties.

Results and discussion

$[Hg(4\text{-}CH_3C_5H_4NO)_6](ClO_4)_2$ was prepared by adding concentrated $HClO_4$ to a slurry of HgO in EtOH (95%) until dissolution was complete. To this, a large excess of the 4-methylpyridine-1-oxide ligand in 95% EtOH was added with the concomitant precipitation of a white solid. The 6:1 adduct (m.p. = 157 — 158 °C) could be recrystallized from acidic EtOH (95%). Metal analysis: Expected: 19.00. Found: 19.70, 18.73. Preparation or recrystallization attempts from neutral solutions yielded undesirable products.

The infrared spectra as mulls of the new compound displayed bands at 1206, 826, 361 (also at 320 and 225) and at 761 cm^{-1} which can be assigned[4,7] to the N–O stretch, N–O bend, Hg–O stretch and ring bend vibrational modes, respectively. Also, a single broad band was observed at 1085 cm^{-1}, indicating uncoordinated perchlorate anion. The X-ray powder patterns were obtained and they contained arcs at the following values of D, the interlattice spacings (in Å, followed by the relative intensity): 5.197(10), 4.781(10), 3.625(6), 3.381(6), 2.925(6), 2.603(4), 2.426(10), 2.256(4), 2.158(3), 1.864(3), 1.812(3), 1.757(3) and 1.711(3). These bands could be indexed in the tetragonal group with $a = b =$ 21.21 Å and $c = 9.33$ Å. Density measurements on this compound yielded a value of 1.4 gm/ml and approximately 4 molecules per unit cell. Conductivity measurements using acetonitrile as solvent indicated that $[Hg(4\text{-}CH_3C_5H_4NO)_6](ClO_4)_2$ is a strong electrolyte in that solvent with equivalent conductances of 165.0, 214.5 and 246.0 cm^2/ohm mol at 3.81×10^{-4}, 3.81×10^{-5} and 7.62×10^{-6} *M*, respectively. The extrapolated equivalent conductance at infinite dilution is 264 cm^2/ohm mol. All of these data, including the shifts in the infrared bands, are quite similar to the data for the pyridine-1-oxide adduct (see for example reference 5) and indicate that the 6:1 adduct of 4-methylpyridine-1-oxide with mercury(II) is indeed a member of the larger family of pyridine-1-oxide complexes with mercury(II) and not an anomaly as previously thought. A comprehensive study of other 6:1 adducts of 4, 3 and 2 substituted pyridine-1-oxides with mercury(II) is being completed.

Acknowledgments

We wish to acknowledge financial support from a George N. Shuster Fellowship and a CUNY–FRAP award.

References

1 R. L. Carlin, *J. Am. Chem. Soc., 83,* 3773 (1961).
2 R. L. Carlin, J. Roitman, M. Dunkleff and S. O. Edwards, *Inorg. Chem., 1,* 182 (1962).
3 J. F. Villa, *Thesis,* University of Miami (1967).
4 A. J. Pappas, *Dissertation,* University of Miami (1969).
5 A. J. Pappas, J. F. Villa and H. B. Powell, *Inorg. Chem., 8,* 550 (1969).
6 I. S. Ahuja and P. Rastogi, *J. Chem. Soc. A,* 378 (1970).
7 G. Costa and V. Galasso, *Atti Accad. Naz. Lincei, Rend. Cl. Sci. Fis. Mat., 37,* 289 (1964).